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COMPARISON OF AMBIENT AIR SAMPLING TECHNIQUES FOR VOLATILE ORGANIC COMPOUNDS

by

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16. ABSTRACT

A series of fourteen experimental sampling runs were carried out at a field site to collect data from several ambient air monitoring methods for volatile organic compounds (VOCs). Ambient air was drawn through a sampling manifold and was continuously spiked with volatile organic compounds to give concentrations 1 to 3 ng/L above background air. The spiked compounds were chloroethene,1,1-dicholorethene, dichloromethane, 3-chloropropene, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, tetra chloromethane, trichloroethene, toluene, tetrachloroethene, chlorobenzene, and 1,2- dimethylbenzene. Special canisters were utilized to collect whole air, time-integrated samples. An automated gas chromatographic system using capillary column separation and multiple detectors was used for analysis. Replicate analysis of the canister samples provided precision data for each detector: ± 3.7% for the six compounds detected by the electron capture detector, ± 7.3% for the same compounds analyzed by the mass selective detector, and ± 7.7% for the flame ionization detector. Tenax GC adsorbent samples were also collected in parallel with the canister samples. These samples were analyzed by standard gas chromatographic/mass spectrometric techniques. For Tenax, precision values ranged from 8 to 16 percent. When comparing measured recoveries with expected concentrations, the canister sampling approach yielded values from 89 to 120 percent. Recoveries, using Tenax adsorbent, ranged from 8-104%.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

Recently an automated gas chromatographic (GC) system employing multiple detectors has been designed and laboratory tested. Emphasis during these tests was placed on the evaluation of system features that can affect sample integrity of volatile organic compounds (VOCs) during reduced temperature preconcentration and subsequent analysis. In the present study the automated GC system was utilized in carrying out a comparison of air sampling techniques. During the sampling period whole air collection into specially treated canisters was compared with Tenax GC sampling techniques. Analysis of the canisters was accomplished with the automated GC system, while a gas chromatograph/mass spectrometer was used to analyze the Tenax samples.

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ABSTRACT

The specific objective of this study was to carry out a comparison of ambient air sampling techniques. A series of fourteen experimental sampling runs were carried out at a field site adjacent to Battelle's chemistry laboratory. Ambient air was drawn through a sampling manifold and was continuously spiked with a mixture of fifteen volatile organic compounds (VOCs) to give concentrations 1 to 3 ng/L above background air. The spiked compounds were chloroethene, 1,1-dichloroethene, dichloromethane, 3-chloropropene, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, tetrachloromethane, trichloroethene, toluene, tetrachloroethene, chlorobenzene, and 1,2-dimethylbenzene.

During the sampling period passivated stainless steel canisters were utilized to collect whole air integrated samples upstream and downstream of the spiking region. An automated gas chromatographic system was employed to analyze the sample canisters. This system uses capillary column separation and multiple detectors for sample analysis (electron capture, flame ionization and mass selective detectors). Replicate analysis of the canister samples with the automated GC system provided precision data for each detector. An average analytical precision of $\pm$ 3.7 percent was found for the six compounds detected by the electron capture detector. A precision of $\pm$ 7.3 percent was obtained for the same six compounds analyzed by the mass selective detector. With the flame ionization detector system a precision value of $\pm$ 7.7 percent was found for these six compounds.

Tenax GC adsorbent samples were also collected downstream of the spiking region in parallel with the integrated canister samples. These samples were analyzed by standard gas chromatographic/mass spectrometric techniques. For Tenax, precision values ranged from 8 to 16 percent. When comparing measured recoveries with expected concentrations, the

canister sampling approach yielded values from 89 to 120 percent. Recoveries, using Tenax adsorbent, ranged from 8 to 104 percent.

This report is being submitted in fulfillment of Contract No. 68-02-3487 by Battelle, Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. It covers a period from February 15, 1984 to December 31, 1984, and work was completed as of December 31, 1984.

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SECTION 1

INTRODUCTION

The Methods Development Branch of the Environmental Monitoring Systems Laboratory (EMSL) is responsible for the development and evaluation of state-of-the-art and emerging analytical techniques for the determination of organic compounds in ambient air. Recently, a priority listing of volatile organics has been established and the EMSL is focusing on further development of analytical methodology associated with the detection of these compounds. Primary emphasis has been placed on developing field-compatible analytical systems.

During the past two years a joint effort by Battelle's Columbus Laboratories and EPA has resulted in the development and evaluation of a prototype system for analysis of sixteen volatile organic compounds (VOCs) (1,2). The system consists of a reduced-temperature trap for condensing organics from whole air, and a capillary column gas chromatograph (GC) with flame ionization (FID) and electron capture detectors (ECD) to quantitatively monitor the VOCs. Software development using the basic programming capability of the GC system permits automatic sampling and analysis to be achieved with minimal operator interfacing. The prototype system has been tested with respect to sample drying procedures (selective removal of water vapor), co-collection of reactive ambient air species, and collection and release efficiency. The prototype design has also been evaluated by comparing two nominally identical systems using calibration mixtures and ambient air. Excellent results were obtained during these laboratory tests and the following recommendations were given:

- The automated GC system should be field tested. During the field tests the reduced temperature trapping system should be compared with other preconcentration techniques such as solid adsorbents and passive dosimeters.

- Many of the target compounds tested in the laboratory also co-elute with other ambient air species. Although the combina-

tion of capillary column and flame ionization and electron capture detectors alleviate some of the identification and quantitation concerns, other more selective detectors are needed. Integrating a mass selective detector into the automated gas chromatographic system is recommended. The increased specificity of this detector over other detection systems will allow better differentiation of co-eluting GC peaks and thus improve present quantitative capability.

This report focuses on the comparison of two ambient air sampling techniques. Specifically, whole air collection into specially treated canisters was compared with Tenax GC adsorbent sampling techniques. Analysis of the canisters was accomplished with the automated GC system while Tenax adsorbent samples were analyzed by standard gas chromatographic mass spectrometric techniques. The comparison study was carried out at a site adjacent to Battelle's chemistry laboratory. To assure detectable concentrations, the sampling manifold was spiked with a mixture of fifteen VOCs and the comparison focused on these compounds. Precision and accuracy estimates for both sampling methods were obtained. Other active and passive sampling devices were also compared during the above field study. However these results are reported elsewhere (3,4).

SECTION 2

CONCLUSIONS

A comparison of whole air collection into specially treated canisters versus Tenax adsorbent sampling has been completed. An automated GC system employed cryogenic preconcentration, a fused silica capillary column, and multiple detectors (electron capture, flame ionization, and a mass selective detector) for canister analysis. Standard gas chromatographic mass spectrometric techniques were used for Tenax adsorbent analyses. A series of fourteen experimental sampling runs was carried out at a field site using ambient air spiked with a mixture of fifteen volatile organic compounds. The significant findings from this study are presented below:

(1) Replicate analysis of canisters collected upstream and downstream of the spiking region with the automated GC system provided precision data for each detector. For concentrations varying from 1 to 70 ng/l an average relative standard deviation (RSD) of $\pm$ 3.7 percent was found for the six compounds detected by the electron capture detector (1,1,2-trichloro-1,2,2-trifluoroethane, trichloromethane, 1,1,1-trichloroethane, tetrachloromethane, trichloroethene, and tetrachloroethene). An RSD of $\pm$ 7.3 percent was obtained for the same six compounds analyzed with the mass selective detector. A similar value of $\pm$ 7.7 percent was found with the flame ionization detector.

(2) The six compounds that were detected by both the electron capture detector (ECD) and mass selective detector (MSD) were intercompared using percent relative difference values [100(ECD response-MSD response)/average response]. Relative difference values ranged from -11.8 percent (1,1,2-trichloro-1,2,2-trifluoroethane) to 36.9 percent (trichloroethene).

(3) Tenax GC adsorbent samples also were collected in parallel with the integrated canister samples and then were analyzed by standard gas chromatographic mass spectrometric techniques. Analysis of duplicate Tenax samples (10 L) resulted in RSD values that ranged from 8 to 16 percent. Recovery relative to canister sampling was as follows: chloroethene and 1,1-dichloroethene (no meaningful data), dichloromethane (83%), 3-chloropropene (87%), 1,1,2-trichloro-1,2,2-trifluoroethane (39%), trichloromethane

(100%), 1,2-dichloroethane (100%), 1,1,1-trichloroethane (130%), benzene (110%), tetrachloromethane (110%), trichloroethene (112%), toluene (70%), tetrachoroethene (88%), chlorobenzene (78%) and 1,2-dimethylbenzene (55%).

SECTION 3

RECOMMENDATIONS

Additional studies should be undertaken under controlled conditions with analytical uncertainties minimized as much as possible by employing the same analysis procedure for all collected samples. Techniques to be compared should include distributive air volume sampling with Tenax adsorbent, passive sampling using personal exposure devices, and whole air collection in canisters.

SECTION 4

EXPERIMENTAL

PREPARATION OF STANDARDS

The target compounds (except for vinyl chloride) were obtained as neat liquids (>98% purity) from Eastman Kodak, Aldrich or Baker Chemical Company. A reference gas mixture was prepared by injecting predetermined amounts of each test compound into an aluminum cylinder that had been previously flushed with high purity air and evacuated. After injection of the neat liquid standards, the cylinder was pressurized to 1200 psig with "hydrocarbon free" air (<0.10 ppm hydrocarbon measured as methane). In order to verify the reference gas concentrations, a second set of reference concentrations were established by injecting an accurately measured quantity of each of the neat compounds into a 17.3 cubic meter Teflon-lined aluminum chamber. After equilibration, a GC response factor was determined for each compound by analysis of a known volume of air using the cryogenic trapping/GC system. This same system was used to analyze the gas cylinder standards and the actual concentrations were calculated using the response factors derived as described above.

Vinyl chloride was obtained from Matheson Gas Products at a concentration of 50 ppmv. A known volume of the commercial standard was injected into the reference cylinder to give a concentration of 1 ppmv.

National Bureau of Standards compressed gas standards for benzene (SRM 1808) and tetrachloroethylene (SRM 1805) were used to verify the accuracy of the reference mixture. In all cases the values determined from the GC analysis agreed within 20 percent of the value calculated from the volume of liquid injected and cylinder pressure. The concentrations of components in the calibration cylinder are listed in Table 1.

In addition, an audit cylinder was provided by EPA, without disclosure of the actual concentration. Component identities and measured concentrations of this mixture were determined and are included in this report.

TABLE 1. CONCENTRATIONS OF TARGET COMPOUNDS IN CALIBRATION CYLINDER

Compound	µg/L(a)
Chloroethene (vinyl chloride)	2.58
1,1 Dichloroethene (vinylidene chloride)	1.70
Dichloromethane (methylene chloride)	1.33
3-Chloropropene (allyl chloride)	1.94
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	3.41
Trichloromethane (chloroform)	2.67
1,2-Dichloroethane	2.42
1,1,1-Trichloroethane (methyl chloroform)	2.97
Benzene	1.47
Tetrachloromethane (carbon tetrachloride)	3.62
Trichloroethene (trichloroethylene)	2.69
Toluene	1.77
Tetrachloroethene (tetrachloroethylene)	3.39
Chlorobenzene	2.20
1,2-Dimethylbenzene (o-xylene)	2.04

(a) At 25°C and 1 atmosphere.

INSTRUMENTATION

The automated cryogenic GC system used for sampling and analysis was composed of two instruments (see Figure 1). Sample collection was accomplished with a modified Nutech Model 320-01 cryogenic unit. The Nutech instrument contained two subsystems. An electronics console was employed for setting and controlling various temperature zones, while the sample handling unit contained the six-port valve and cryogenic trapping components. Three temperature zones were controlled by the console and include the valve, trap, and transfer (fittings) lines. The valve and transfer lines were maintained at 120°C. During sample collection the trap temperature was regulated by the electronics console, which controlled the release of liquid nitrogen via a solenoid valve. During the current study the temperature setpoint of the trap during sample collection was -160°C $\pm$ 5°C. A cylindrically coiled 250 watt heater was used to heat the trap during the sample desorption cycle. The trap was wrapped around the heater to promote heat transfer during the desorption cycle (-160°C to 120°C in 60 sec). Rapid heating of the trap provided efficient transfer of the sample components onto the gas chromatographic column. The sample trap was constructed of 20 cm by 0.2 cm i.d. stainless steel tubing packed with silanized glass beads (60/80 mesh). A Seiscor six-port air-actuated valve (Seismograph Service Corp., Tulsa, OK) was used to facilitate sample collection and injection.

Sample analysis was achieved with a Hewlett Packard Model 5880A (Level 4) gas chromatograph equipped with flame ionization and electron capture detectors. A mass selective detector (Hewlett Packard Model 5970) was also interfaced to the gas chromatographic system. A 50 m by 0.32 mm i.d., OV-1 fused silica column (Hewlett Packard) was used to resolve the target compounds. The column flow was maintained at 4 mL/min with a mass flow controller (Tylan MC-260). Zero grade helium (Matheson) served as the carrier gas, and zero grade nitrogen (Matheson) was used as the make-up gas to provide proper electron capture operation. Optimum analytical results were achieved by temperature programming the gas chromatographic column from -50°C to 150°C at 8°/min. The column exit flow was split (50/50) using a low dead-volume union with a two-hole

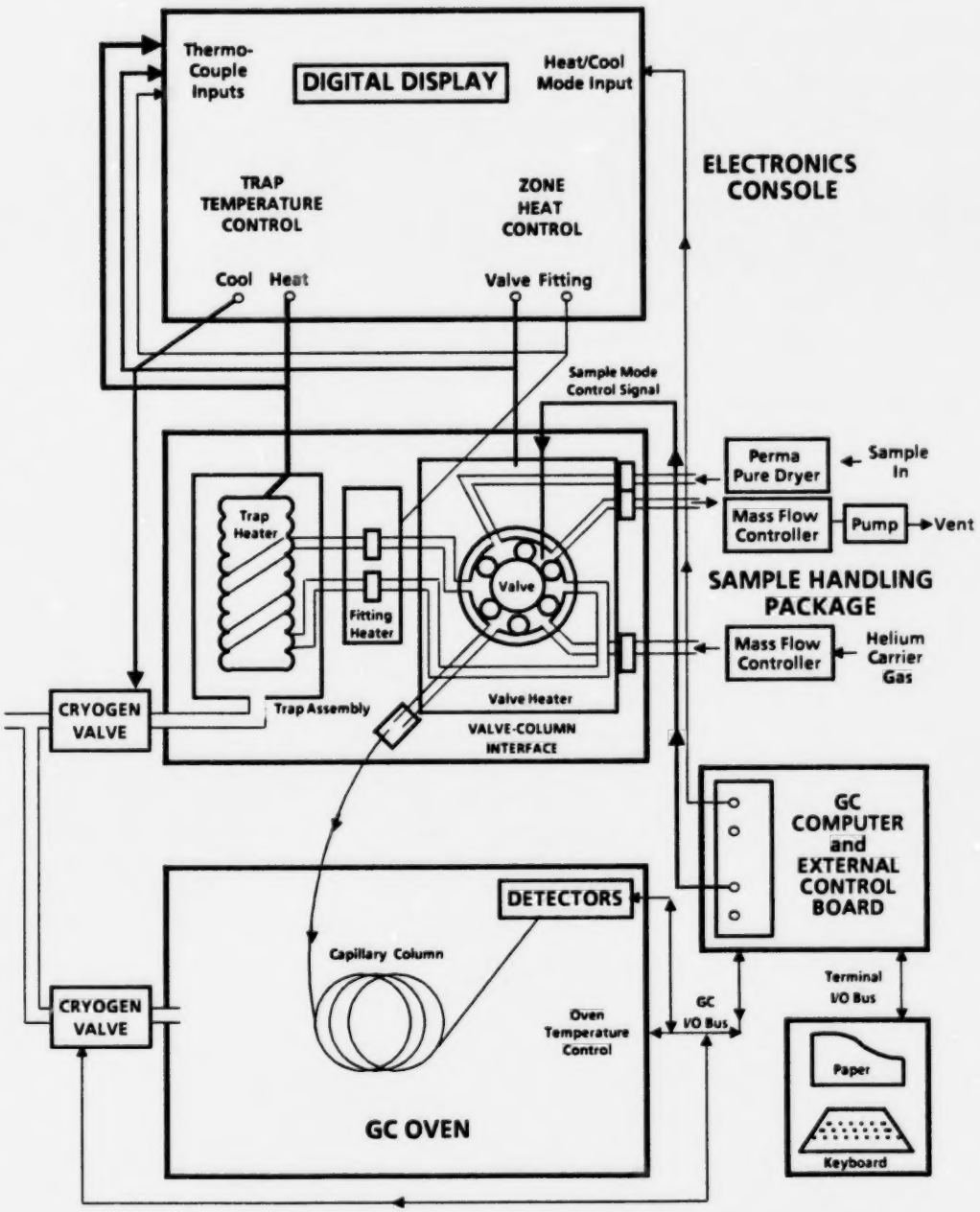

Figure 1. Block diagram of automated GC sampling and analysis system.

ferrule. One portion of the flow was directed to the mass selective detector. The remaining flow passed through the electron capture and flame ionization detectors which were connected in series.

A Perma Pure dryer (Model MD-125-48F) with a tubular hygroscopic ion-exchange membrane (Nafion) was used to remove water vapor selectively from mixed gas streams. The dryer was purchased in a shell and tube configuration. The tube size was 30 cm by 0.1 cm i.d. and was imbedded within a shell of Teflon tubing of 0.25 cm i.d. Sample flow through the tube was maintained at 10 mL/min with a mass flow controller (Tylan MC-260). A counter-current flow of dry zero air (200 mL/min) was used to purge the shell.

A gas-phase dynamic dilution system (Columbia Scientific Industries) was employed to generate ppb mixtures of the target compounds. Ultra-zero air (Matheson) was the diluent gas. Internal mass flow controllers provided accurate gas flows, which were verified with a soap-film bubble meter.

PROCEDURE

Sampling Manifold

In order to obtain a uniform air sample for each of the sampling and analysis techniques, a glass manifold (Ace Glass Company) was used as shown in Figure 2. The manifold contained a 5 ft sampling inlet which extended through the roof of the mobile laboratory. Inside the laboratory the inlet was connected sequentially to a 76 mm glass filter holder, a 3 ft mixing chamber and a 3 ft sampling chamber. A variable speed pump and dry test meter were used to maintain a flow of 50 L/min through the manifold. A rotameter was placed into the system to provide a visual check of the flow rate. A quartz fiber filter (QAST 2500) was inserted into the filter holder to remove particles from ambient air. The mixing chamber was modified at Battelle to permit the spiking of ambient air with known amounts of air from a calibration cylinder (Table 1). To verify that complete mixing occurred prior to the sampling chamber, NO (1.0 ppm) was injected into the mixing chamber via the gas dilution system.

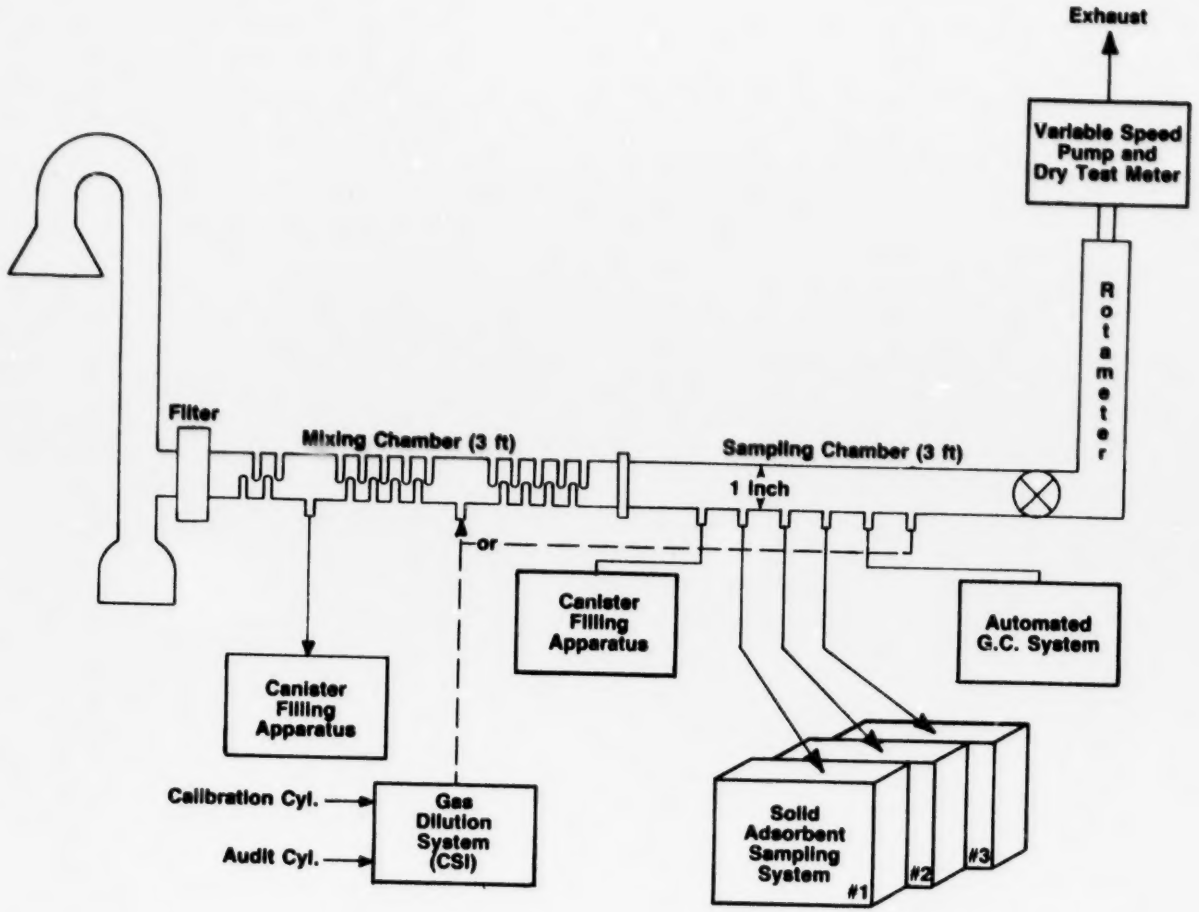

Figure 2. Diagram of sampling manifold and instrumentation employed during field program.

An NO analyzer was used to radially probe the various sampling ports to assure complete mixing.

For normal sampling periods incoming ambient air was spiked with a calibration mixture (50.0 mL/min) from the gas dilution system. To operate the gas dilution system, a flow of ultra-zero air (1.00 L/min) was also required. For several of the sampling periods calibration or audit mixtures were backflushed through the manifold to generate known calibration mixtures. To carry out this task the gas dilution flow from the CSI unit was diverted from the mixing chamber to the sampling chamber. Likewise the pump and ball valve were shut off so that the flow exited through the mixing chamber. During these tests the calibration/audit flow was 50.0 mL/min while the air flow was maintained at 5.00 L/min (0.0099 dilution).

Sampling Protocol

Fourteen test runs were carried out at the field site. Eleven sampling runs were made with spiked ambient air while the remaining three runs involved the injection of calibration mixtures (two with the audit cylinder/one with Battelle's calibration cylinder). The test runs usually were started at 1:00 p.m. and each lasted two hours. During the two hour sampling period two canisters and three solid adsorbent sampling systems were used to collect time integrated air samples. The automated GC system collected two fifty minute integrated samples during this time. The operational procedure for these sampling systems follows.

Canister Filling Apparatus

Two 6-liter stainless steel canisters (Demaray Scientific Instrument, Ltd., Pullman, WA) were used for collecting integrated whole air samples. One canister was positioned upstream, the other can was placed downstream, of the spiking inlet. In preparation for sampling, each canister was sequentially filled (15 psig) and evacuated (25" Hg) five times using ultra zero air as the flushing gas. After the fifth evacuation the canister was sealed, transferred to a higher vacuum system and pumped down to 0.1 torr. A liquid nitrogen trap was utilized in this system to prevent organics originating in the pump oil from back-streaming into the can.

Following the final evacuation each canister was connected to the appropriate filling apparatus. Figure 3 illustrates a diagram of the canister filling apparatus. A stainless steel pump (Metal Bellows Corp., Model MB-155) directed flow to the sample canister. A stainless steel tube restrictor (0.03 inch i.d. by 6 inch length) was positioned upstream of the mass flow controller (Tylan MC-260) to prevent pump oscillations from affecting the mass flow. An adjustable relief valve was positioned between the pump and mass flow controller (MFC) to provide a continuous throughput of sample air. The mass flow controller was maintained at 80 mL/min during sampling. At this flow rate a canister would fill to ~9 psig after a two hour collection period. This pressure provided sufficient sample in the cans so that replicate analyses could be accomplished with the GC system. Prior to the test runs, the canister filling apparatus was checked by several experiments that simulated actual sampling conditions using ultra-zero air. No contamination was observed.

Solid Adsorbent Sampling System

Tenax GC adsorbent tubes were collected using the system shown in Figure 4. Each mass flow controller was adjusted so that nominal sample volumes of 5, 10 (duplicate), and 20 liters were collected over a two-hour period. The adsorbent tubes were leak checked immediately before sampling by sealing the inlet line and initiating sample collection (i.e. pump on). A leak-free system was indicated by a zero reading on the mass flow controller. Sample blanks were obtained by removing a blank cartridge from its storage container, placing it in line, and repeating the leak check procedure. The blank was then immediately returned to its container. All sample and blank adsorbent tubes were stored in sealed metal cans containing activated charcoal. Tenax GC adsorbent tubes used by Battelle consisted of packed glass cartridges as described for the Volatile Organic Sampling Train (VOST) System developed by EPA for stack sampling (6). Sample analysis was completed within 48 hours of collection. The operating and analytical procedures are described fully in a companion report (3).

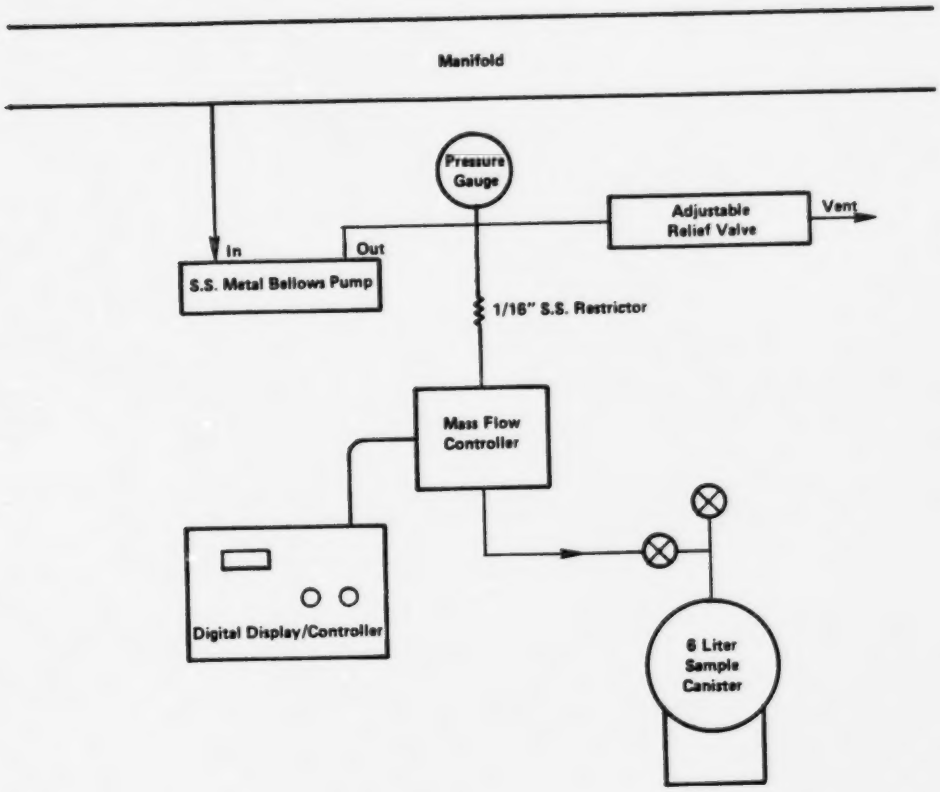

Figure 3. Diagram of canister filling apparatus.

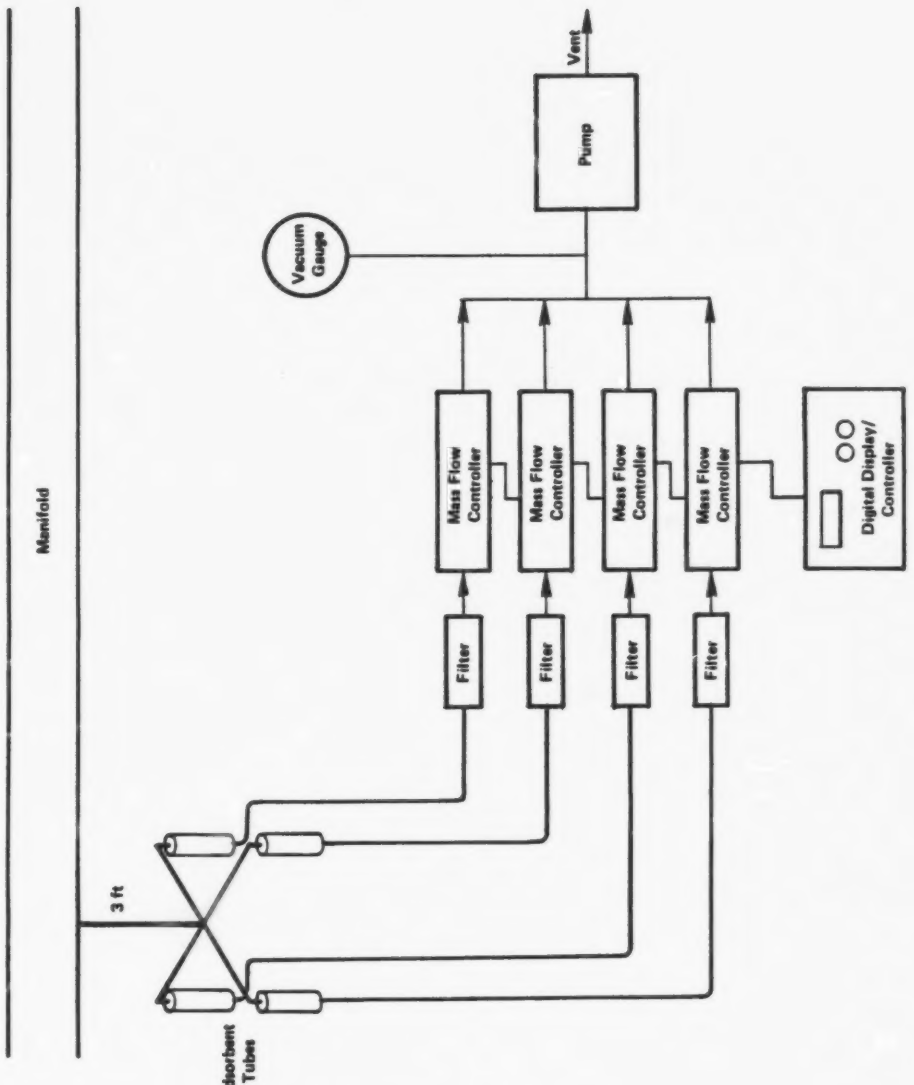

Figure 4. Diagram of solid adsorbent sampling system.

Automated GC System

The automated GC system was programmed to collect and immediately analyze time integrated samples. Two "real time" integrated samples were collected during each two-hour test run. Software was developed to provide for the extended time coverage during the real-time field sampling. Time coverage is defined as the ratio of sample collection time to the total run time. In the program total run time is composed of the 50 minute analysis time plus a "post run" time between analyses. The "post run" time is an input parameter in the program and is currently set to 10 minutes. This setting provides the needed time for oven temperature recycling to occur and for the analytical report to be printed and transferred to tape. Sample collection actually begins 10 minutes into the analysis cycle and extends throughout the "post run" period. Thus 50 minutes of the total run time of 60 minutes is spent in collecting a sample i.e. 83 percent time coverage. Likewise with the current program the operator does not have to be present to initiate sampling. He must indicate the number of samples to be processed and then must specify the start time (24 hour clock). As currently programmed, the first sample collection will commence 20 minutes after the specified start time.

In order for the analysis phase of the program to begin all GC heating zones must be at their temperature set points. Unfortunately the MSD interface heating zone ("INJ 2 TEMP") would not maintain a constant temperature. A 15 minute cycling of $\pm$ 10^{o}C was observed at a set point of 250^{o}C. This fluctuation did not affect the chromatography but it did delay the start of the GC program which resulted in variable sample collection times. To circumvent this problem several program commands were written to turn off the MSD interface zone just prior to the sample injection and to restore the zone heat immediately after injection.

Figure 5 shows a diagram of sample flow to the GC system during the collection and analysis cycle. During the collection cycle a stainless steel pump (Metal Bellows, Corp., Model MB-155) pulled manifold air through the Perma Pure dryer and into the cryogenic trap (-160^{o}C). A mass flow controller (Tylan MC-260) maintained this flow at 10.0 mL/min. During the analysis cycle helium gas (4.00 mL/min) carried the sample components

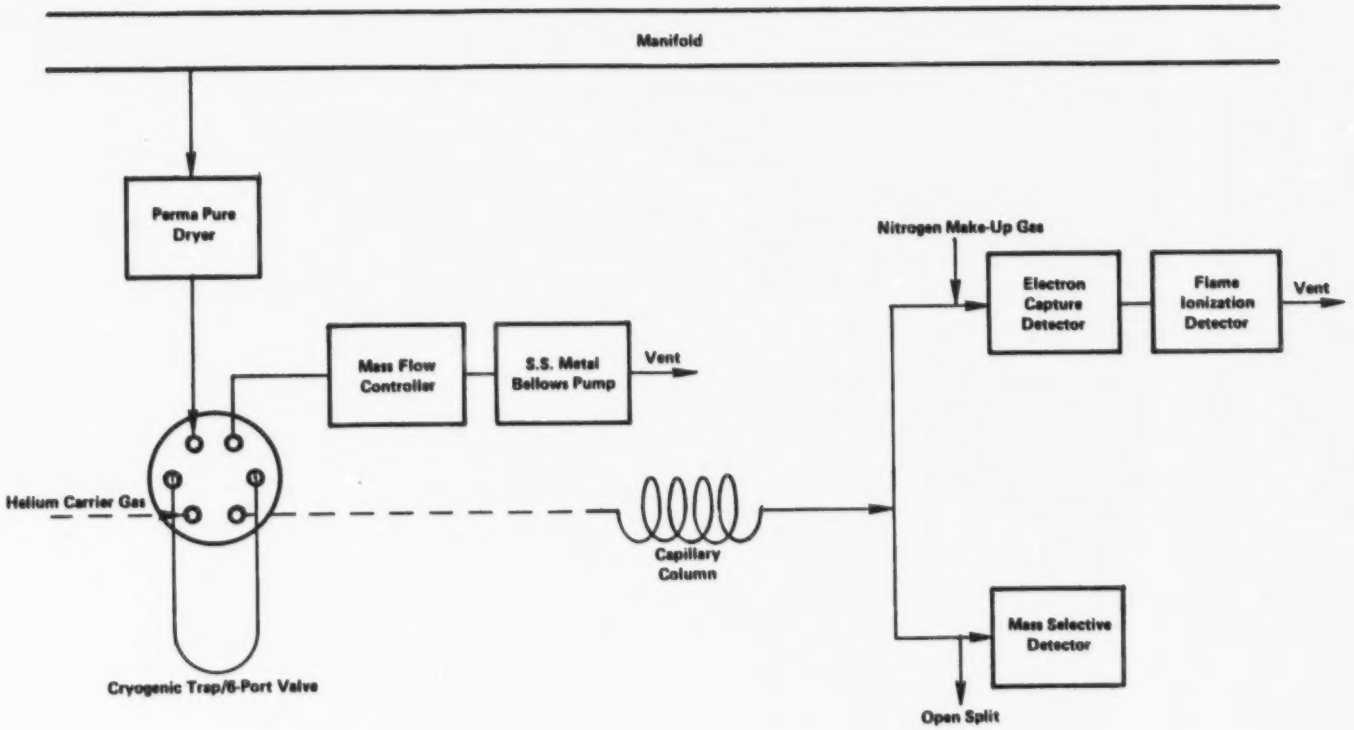

Figure 5. Flow diagram of GC system during sampling and analysis.

through the heated trap (120°C), to the analytical column, and into the various detectors. The flow to the mass selective detector was 2 mL/min. Since the MSD system required 0.8 mL/min in the open split mode of operation, the excess flow was vented through the open split. Nitrogen make-up gas (50 mL/min) served as a good compromise flow to insure proper operation of both the electron capture and flame ionization detectors, which were connected in series. The connection of the two detectors in series resulted in additional peak broadening in the FID unit (when compared to the operation of both detectors in parallel). However peak broadening effects did not change the quantitative results.

The mass selective detector was utilized in the selected ion monitoring (SIM) mode of operation during the field study. In this mode of operation the software permitted up to six mass ions to be monitored repetitively. In order to maximize the number of compounds that could be quantified with the unit, two groups of six ions were utilized and are listed in Table 2. The compounds associated with these mass ions, along with GC retention times and detector operating conditions are also shown in Table 2. For real time sampling the group 1 mass ions were utilized with the data acquisition segment of the program and quantitative procedures were carried out with the system's software. For the canister samples, duplicate analyses were performed using group 1 ions followed by a single analysis using group 2 ions.

TABLE 2. TARGET COMPOUNDS EXAMINED WITH MASS SELECTIVE DETECTOR SYSTEM(a)

Group No.	Compound	Retention Time (min)	Ion Monitored (mass to charge ratio)	Dwell Time (milliseconds)
1	1,1,2-Trichloro-1,2,2-trifluoroethane	7.36	151	50
	Trichloromethane	8.49	83	50
	1,1,1-Trichloroethane	8.95	97	50
	Tetrachloromethane	9.24	117	50
	Trichloroethene	9.70	130	50
	Tetrachloroethene	11.22	166	50
2	Chloroethene	4.56	62	50
	1,1-Dichloroethene	6.99	96	50
	Dichloromethane	7.16	84	50
	3-Chloropropene	7.23	76	50
	1,2-Dichloroethane	8.84	62	50
	Benzene	9.17	78	50
	Chlorobenzene	11.59	112	50

(a) Electron multiplier = 1400 Kv, peak width window = 1.0 amu.

SECTION 5

RESULTS AND DISCUSSION

OVERVIEW

The comparison study was carried out at a field site adjacent to Battelle's chemistry laboratory. The evaluation study consisted of fourteen sampling runs as listed in Table 3. Runs 4 and 11 were clean air experiments using dilution mixtures from an audit cylinder supplied by EPA, while run 5 was a similar run using Battelle's calibration cylinder. The remaining sampling runs were made with spiked ambient air. The analytical precision of the three detectors from the automated GC system was obtained by replicate analysis of canisters collected from the sampling manifold during the tests. A comparison was also made of concentrations of the six target compounds that were detected by both the electron capture and mass selective detector. Whole air canister concentrations determined by the cryogenic GC system (using the mass selective detector response) were also compared with those values obtained from Tenax GC adsorbent devices.

ANALYTICAL PRECISION OF MSD, ECD, AND FID DETECTORS

An estimate of the analytical precision of the cryogenic GC system was determined from triplicate analyses of spiked and background canisters collected during each sample period. Due to the limitation in the number of ions monitored with the mass selective detector, duplicate MSD analyses were made on the six compounds listed in Table 2 as Group 1 ions while a single analysis was carried out on the Group 2 compounds. Triplicate analyses of the same six Group 1 compounds were carried out with the ECD and FID detectors. Another set of six compounds was quantified with the FID unit during each analysis. Tables 4 and 5 show the data from the spiked and background canisters. Both tables list by run number

TABLE 3. LIST OF SAMPLING RUNS

Run No.	Sampling Date	Description
1	7/12/84	Ambient Air (Trial Run)
2	7/17/84	Ambient Air
3	7/19/84	Ambient Air
4	7/20/84	Audit Cylinder
5	7/24/84	Calibration Cylinder
6	7/26/84	Ambient Air
7	7/27/84	Ambient Air
8	7/30/84	Ambient Air
9	7/31/84	Ambient Air
10	8/02/84	Ambient Air
11	8/03/84	Audit Cylinder
12	8/06/84	Ambient Air
13	8/07/84	Ambient Air
14	8/09/84	Ambient Air

TABLE 4. MEAN CONCENTRATIONS (ng/L) AND RELATIVE STANDARD DEVIATIONS (%) OF TARGET COMPOUNDS FROM SPIKED CANISTERS AS DETERMINED WITH THE MSD, ECD, AND FID DETECTORS

	RUN NUMBER	FREON 113 MSD.MEAN	FREON 113 MSD.RSD	CHLORO-FORM MSD.MEAN	CHLORO-FORM MSD.RSD	1,1,1-TRI CHLOR. MSD.MEAN	1,1,1-TRI CHLOR. MSD.RSD	CARB. TETR CHLORIDE MSD.MEAN	CARB. TETR CHLORIDE MSD.RSD	TRICHLORO ETHYLENE MSD.MEAN	TRICHLORO ETHYLENE MSD.RSD	PERCHLORO ETHYLENE MSD.MEAN	PERCHLORO ETHYLENE MSD.RSD	AVERAGE RELATIVE STD.DEV
	2	10.3	13.7	2.8	0.0	32.0	4.4	4.9	2.8	3.3	4.3	5.2	2.7	4.7
	3	.	.	4.7	3.0	85.0	1.7	5.3	2.7	3.8	3.7	8.1	1.7	2.8
	4	.	.	7.8	9.1	.	.	20.7	9.6	.	.	8.0	8.8	9.2
	5	79.4	.	27.1	.	34.8	.	37.2	.	23.7	.	40.0	.	.
	6	18.3	.	9.0	.	84.0	.	4.4	.	3.8	.	5.5	.	.
M	7	24.6	.	3.8	.	4.5	.	4.0	.	4.6	.	6.1	.	.
S	8	8.5	0.8	4.1	1.7	9.2	0.8	3.6	15.7	3.7	5.7	4.8	8.8	5.8
D	9	15.3	14.8	4.7	12.0	22.0	10.3	4.0	0.0	2.7	7.9	3.7	0.0	7.5
	10	11.3	8.8	3.1	9.1	28.8	14.8	3.7	7.8	4.2	8.7	4.8	5.9	8.8
	11	.	.	7.0	10.1	.	.	14.9	3.8	.	.	5.8	1.3	5.1
	12	14.8	8.8	4.7	9.0	19.5	5.1	4.9	8.7	14.3	11.9	9.3	.	8.3
	13	11.8	3.6	4.6	12.3	12.4	17.1	5.0	11.3	2.7	15.7	5.7	2.5	10.4
	14	12.2	22.0	4.8	6.5	18.8	15.8	4.1	2.1	5.1	2.8	7.3	.	9.8
	0	20.4	10.1	6.8	7.3	30.1	8.7	9.0	6.4	8.5	7.3	8.8	4.0	

	RUN NUMBER	FREON 113 ECD.MEAN	FREON 113 ECD.RSD	CHLORO-FORM ECD.MEAN	CHLORO-FORM ECD.RSD	1,1,1-TRI CHLOR. ECD.MEAN	1,1,1-TRI CHLOR. ECD.RSD	CARB. TETR CHLORIDE ECD.MEAN	CARB. TETR CHLORIDE ECD.RSD	TRICHLORO ETHYLENE ECD.MEAN	TRICHLORO ETHYLENE ECD.RSD	PERCHLORO ETHYLENE ECD.MEAN	PERCHLORO ETHYLENE ECD.RSD	AVERAGE RELATIVE STD.DEV
	2	9.6	25.0	4.7	15.0	33.0	4.3	8.5	1.7	4.3	3.3	5.2	2.7	8.7
	3	.	.	5.8	2.4	87.0	0.4	10.1	1.4	6.6	2.1	8.2	1.7	1.6
	4	.	.	7.9	3.6	.	.	29.6	0.0	.	.	8.5	8.7	3.4
	5	65.2	21.5	25.5	3.5	30.2	8.9	34.4	.	28.4	0.0	33.5	.	8.5
	6	15.2	1.3	12.1	6.6	70.7	0.0	8.9	0.0	5.2	5.8	5.8	1.7	2.6
E	7	16.5	45.4	4.6	1.5	5.2	2.7	4.6	0.0	3.9	0.0	4.4	0.0	8.3
C	8	7.1	0.0	4.6	4.3	10.8	0.0	4.3	2.8	4.1	0.0	4.8	1.3	1.4
D	9	16.1	1.9	5.9	6.6	25.6	0.8	4.4	1.8	3.9	3.1	4.1	2.0	2.7
	10	11.5	1.2	3.8	3.7	25.5	0.5	4.3	0.5	3.9	3.1	4.5	0.4	1.6
	11	.	.	6.6	1.7	.	.	16.6	2.4	.	.	5.6	0.4	1.5
	12	12.3	1.1	4.3	1.2	18.0	0.6	5.1	0.6	14.5	4.6	6.9	0.7	1.5
	13	10.5	1.0	5.3	3.6	13.4	2.2	5.0	2.0	4.3	4.7	6.3	1.6	2.5
	14	10.7	2.6	4.2	1.9	19.9	1.5	4.1	1.7	5.7	3.5	6.6	1.2	2.1
	0	17.5	10.1	7.3	4.3	29.0	2.0	10.6	1.3	7.7	2.6	8.0	1.7	

	RUN NUMBER	VINYL CHLORIDE FID.MEAN	VINYL CHLORIDE FID.RSD	FREON 113 FID.MEAN	FREON 113 FID.RSD	CHLORO-FORM FID.MEAN	CHLORO-FORM FID.RSD	1,2 DICHLR ETHANE FID.MEAN	1,2 DICHLR ETHANE FID.RSD	1,1,1-TRI CHLOR. FID.MEAN	1,1,1-TRI CHLOR. FID.RSD	BENZENE FID.MEAN	BENZENE FID.RSD
	2	.	.	.	.	99.0	1.4	16.1	5.3	35.2	2.8	7.7	0.0
	3	.	.	.	.	225.0	0.6	35.2	0.4	94.4	0.4	377.0	0.4
	4	.	.	.	.	.	.	.	.	.	.	15.5	1.8
	5	24.7	1.8	72.0	28.4	29.0	4.1	28.0	2.3	31.6	1.9	16.8	1.2
	6	.	.	19.9	1.5	195.0	0.0	22.7	2.6	79.7	0.8	68.0	0.0
F	7	1.9	14.9	18.4	43.0	20.9	8.8	.	.	4.8	0.0	5.0	1.4
I	8	1.9	5.3	10.3	0.8	165.8	0.2	14.2	0.3	11.6	0.7	4.8	2.0
D	9	2.3	4.3	21.5	0.7	1719.4	0.3	34.2	1.5	33.6	9.8	6.1	0.7
	10	.	.	17.8	1.7	117.0	0.9	143.1	0.8	28.4	1.8	5.0	1.0
	11	8.2	7.3	.	.	7.0	7.1	.	.	.	.	11.3	1.8
	12	2.7	5.6	.	.	.	.	19.7	5.6	23.8	5.0	7.7	7.8
	13	.	.	14.9	3.2	108.4	9.3	21.3	0.5	14.6	2.7	73.0	0.1
	14	2.4	12.5	16.2	3.1	155.2	3.2	29.6	18.9	28.7	14.2	9.2	2.2
	0	8.3	7.4	23.9	10.0	258.2	3.3	36.2	3.6	35.9	3.6	48.7	1.6

	RUN NUMBER	CARB. TETR CHLORIDE FID.MEAN	CARB. TETR CHLORIDE FID.RSD	TRICHLORO ETHYLENE FID.MEAN	TRICHLORO ETHYLENE FID.RSD	TOLUENE FID.MEAN	TOLUENE FID.RSD	PERCHLORO ETHYLENE FID.MEAN	PERCHLORO ETHYLENE FID.RSD	CHLORO-BENZENE FID.MEAN	CHLORO-BENZENE FID.RSD	O-XYLENE FID.MEAN	O-XYLENE FID.RSD	AVERAGE RELATIVE STD.DEV
	2	.	.	10.0	5.7	15.8	0.0	7.9	3.6	2.7	0.0	8.9	10.2	3.2
	3	.	.	43.9	18.0	22.5	1.9	14.0	7.1	3.7	3.8	7.7	1.8	3.8
	4	.	.	.	.	.	.	8.6	0.0	.	.	.	.	0.9
	5	38.7	1.0	29.7	3.0	20.1	1.5	38.2	0.8	25.5	0.4	23.8	1.3	3.8
	6	27.7	27.4	8.4	0.0	20.3	3.0	8.4	3.6	2.6	3.8	8.0	6.7	4.5
F	7	.	.	5.2	10.9	12.0	5.9	7.6	0.9	2.7	7.9	4.5	1.6	9.5
I	8	.	.	6.6	2.7	12.1	0.2	8.1	2.5	2.8	1.8	53.0	0.3	1.5
D	9	16.2	3.1	15.6	12.2	14.6	1.0	7.1	0.7	2.4	5.0	4.8	4.2	3.6
	10	288.7	0.8	16.6	10.2	16.6	0.3	8.1	1.0	2.9	1.4	6.7	10.4	2.7
	11	.	.	.	.	.	.	6.3	3.2	.	.	.	.	4.9
	12	.	.	.	.	21.1	0.7	11.2	7.1	.	.	7.9	8.9	5.8
	13	8.0	9.1	28.2	1.5	21.8	1.4	14.1	2.8	4.1	2.4	8.8	11.2	4.0
	14	24.4	44.7	16.7	55.1	20.1	4.5	13.1	1.5	3.7	2.7	8.0	17.5	14.8
	0	87.3	14.4	17.9	11.9	17.9	1.8	11.7	2.7	5.3	2.9	12.6	6.7	

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TABLE 5. MEAN CONCENTRATIONS (ng/L) AND RELATIVE STANDARD DEVIATIONS (%) OF TARGET COMPOUNDS FROM BACKGROUND CANISTERS AS DETERMINED WITH THE MSD, ECD, AND FID DETECTORS

	RUN NUMBER	FREON 113 MSD.MEAN	FREON 113 MSD.RSD	CHLORO-FORM MSD.MEAN	CHLORO-FORM MSD.RSD	1,1,1-TRI CHLOR. MSD.MEAN	1,1,1-TRI CHLOR. MSD.RSD	CARB. TETR CHLORIDE MSD.MEAN	CARB. TETR CHLORIDE MSD.RSD	TRICHLORO ETHYLENE MSD.MEAN	TRICHLORO ETHYLENE MSD.RSD	PERCHLORO ETHYLENE MSD.MEAN	PERCHLORO ETHYLENE MSD.RSD	AVERAGE RELATIVE STD.DEV
	2	9.4	13.5	0.9	0.0	31.0	4.8	4.1	8.9	0.7	20.2	1.1	0.0	7.5
	3	42.0	.	1.5	.	81.0	.	1.2	.	1.7	.	3.1	.	.
	4	.	.	.	.	.	.	.	.	.	.	.	.	.
	5	.	.	.	.	.	.	.	.	.	.	.	.	.
	6	9.5	.	8.0	.	74.0	.	0.9	.	1.3	.	.	.	.
M	7	1.5	.	1.1	.	3.2	.	0.9	.	0.8	.	1.0	.	.
	8	.	.	.	.	.	.	.	.	.	.	.	.	.
S	9	11.8	.	2.4	.	22.8	.	0.8	.	0.5	.	0.5	.	.
D	10	6.1	.	0.8	.	28.0	.	0.8	.	0.7	.	0.8	.	.
	11	.	.	.	.	.	.	.	.	.	.	.	.	.
	12	6.7	6.3	0.8	8.8	17.8	5.8	1.1	6.4	12.5	5.7	2.3	3.1	6.0
	13	8.3	11.2	4.5	28.3	10.4	3.4	2.0	1.4	1.1	0.0	1.9	3.7	8.0
	14	7.3	.	5.4	.	19.4	.	3.0	.	3.4	.	4.0	.	.
	0	11.2	10.4	2.8	12.4	31.9	4.5	1.8	4.9	2.5	8.8	1.8	2.3	

	RUN NUMBER	FREON 113 ECD.MEAN	FREON 113 ECD.RSD	CHLORO-FORM ECD.MEAN	CHLORO-FORM ECD.RSD	1,1,1-TRI CHLOR. ECD.MEAN	1,1,1-TRI CHLOR. ECD.RSD	CARB. TETR CHLORIDE ECD.MEAN	CARB. TETR CHLORIDE ECD.RSD	TRICHLORO ETHYLENE ECD.MEAN	TRICHLORO ETHYLENE ECD.RSD	PERCHLORO ETHYLENE ECD.MEAN	PERCHLORO ETHYLENE ECD.RSD	AVERAGE RELATIVE STD.DEV
	2	8.1	1.7	0.8	17.7	30.0	0.0	2.5	5.7	1.4	0.0	1.1	0.0	4.2
	3	37.4	.	2.5	.	67.0	.	2.3	.	3.4	.	3.4	.	.
	4	.	.	.	.	.	.	.	.	.	.	.	.	.
	5	.	.	.	.	.	.	.	.	.	.	.	.	.
	6	9.8	0.0	9.2	0.0	70.0	0.0	2.0	0.0	2.0	0.0	1.4	0.0	0.0
E	7	1.4	10.1	1.5	4.7	2.9	4.9	1.0	0.0	1.0	7.1	0.9	7.9	5.8
C	8	1.8	9.4	2.9	14.8	9.3	3.2	0.9	4.7	1.4	10.1	1.1	0.0	7.0
D	9	11.4	0.2	3.3	0.4	23.8	0.8	0.9	0.5	1.0	2.8	0.7	2.0	1.1
	10	8.1	2.8	1.3	4.4	23.1	.	0.9	0.0	1.1	1.3	1.0	4.2	2.8
	11	.	.	.	.	.	.	.	.	.	.	.	.	.
	12	8.3	0.7	0.7	18.2	18.2	0.4	1.0	1.4	12.7	0.2	1.9	1.5	3.4
	13	5.5	2.8	2.5	17.0	11.4	2.5	1.8	0.0	1.5	0.0	2.4	0.0	3.7
	14	5.5	7.7	1.1	7.7	18.9	4.5	1.0	2.8	3.1	2.7	3.5	0.4	4.3
	0	9.3	3.9	2.8	9.2	27.3	2.0	1.4	1.7	2.9	2.7	1.7	1.8	

	RUN NUMBER	FREON 113 FID.MEAN	FREON 113 FID.RSD	CHLORO-FORM FID.MEAN	CHLORO-FORM FID.RSD	1,2 DICHLR ETHANE FID.MEAN	1,2 DICHLR ETHANE FID.RSD	1,1,1-TRI CHLOR. FID.MEAN	1,1,1-TRI CHLOR. FID.RSD	BENZENE FID.MEAN	BENZENE FID.RSD	CARB. TETR CHLORIDE FID.MEAN	CARB. TETR CHLORIDE FID.RSD
	2	.	.	110.0	0.0	18.8	0.9	34.0	4.2	7.8	1.8	.	.
	3	41.0	.	222.0	.	33.0	.	84.0	.	370.0	.	91.0	.
	4	.	.	.	.	.	.	.	.	.	.	.	.
	5	.	.	.	.	.	.	.	.	.	.	.	.
	6	14.0	1.0	198.0	0.7	20.0	0.0	78.0	1.8	87.0	2.1	21.0	8.7
	7	.	.	19.3	.	10.3	.	.	.	3.9	.	.	.
F	8	4.8	2.5	171.1	1.8	12.0	0.8	9.8	0.9	3.4	0.0	.	.
I	9	18.4	0.2	1783.3	0.1	32.0	0.2	28.8	0.5	4.8	1.8	79.4	0.5
D	10	10.9	53.2	109.7	3.1	145.4	1.8	38.2	7.8	5.2	12.0	251.2	0.2
	11	.	.	.	.	.	.	.	.	.	.	.	.
	12	.	.	.	.	17.8	2.4	18.5	3.1	5.5	2.8	.	.
	13	31.4	7.2	97.7	2.5	21.8	0.8	14.5	0.7	5.8	3.0	22.7	33.8
	14	5.3	48.0	148.7	2.9	23.0	2.7	23.0	4.3	7.9	5.4	38.9	34.2
	0	17.7	18.7	317.8	1.8	33.2	1.1	37.8	2.9	48.1	3.8	84.0	15.1

	RUN NUMBER	TRICHLORO ETHYLENE FID.MEAN	TRICHLORO ETHYLENE FID.RSD	TOLUENE FID.MEAN	TOLUENE FID.RSD	PERCHLORO ETHYLENE FID.MEAN	PERCHLORO ETHYLENE FID.RSD	CHLORO-BENZENE FID.MEAN	CHLORO-BENZENE FID.RSD	O-XYLENE FID.MEAN	O-XYLENE FID.RSD	AVERAGE RELATIVE STD DEV
	2	2.8	10.1	17.0	2.5	5.1	2.8	.	.	5.0	8.5	3.8
	3	20.0	.	22.0	.	10.0	.	0.9	.	5.4	.	.
	4	.	.	.	.	.	.	.	.	.	.	.
	5	.	.	.	.	.	.	.	.	.	.	.
	6	.	.	19.0	0.0	4.7	0.0	.	.	4.2	0.0	1.4
F	7	.	.	5.1	.	2.1	.	.	.	2.6	.	.
I	8	.	.	10.4	0.4	4.8	0.0	.	.	3.2	0.4	0.8
D	9	14.8	0.1	13.4	0.2	3.4	12.5	.	.	3.2	7.1	2.3
	10	18.0	3.5	15.5	1.8	5.5	20.8	0.4	39.3	5.8	15.2	14.4
	11	.	.	.	.	.	.	.	.	.	.	.
	12	.	.	18.8	0.4	5.2	0.0	.	.	4.8	0.0	1.4
	13	22.2	8.9	20.8	5.4	10.3	1.4	1.2	0.0	8.1	7.0	8.4
	14	19.0	13.4	17.8	3.2	9.2	4.8	1.1	8.4	8.3	1.3	11.5
	0	15.8	7.2	18.0	1.7	8.0	5.2	0.9	15.2	4.8	4.9	

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the mean concentration (nanograms/liter) and relative standard deviation (%) for each compound. The relative standard deviations (RSD) shown in Tables 4 and 5 are calculated standard deviations divided by the mean concentrations and multiplied by 100 to give percentages. These RSD values are utilized as a direct measure of the analytical precision of each detector. Compounds quantified with the MSD are listed first, followed by the ECD and then the FID responding species. The average concentration and relative standard deviation for each compound over the thirteen sampling days is shown next to run number zero. Daily average relative standard deviations for all compounds quantified by each detector are listed in the last column.

A summary of the analytical precision of all three detectors is shown in Table 6. In viewing the spiked canister data set, an average analytical precision of $\pm$ 7.3 percent was found for the six compounds analyzed with the MSD. Tetrachloroethene had the lowest RSD value ($\pm$ 4.0%) while Freon-113 displayed the highest RSD value ($\pm$ 10.1%). A significantly lower average RSD value of $\pm$ 3.7 percent was obtained for the same six compounds analyzed with the ECD. The RSD values ranged from $\pm$ 1.3 percent (tetrachloromethane) to $\pm$ 10.1 percent (Freon-113). With the FID detector system an average RSD value ($\pm$ 7.7%) similar to the MSD was found. However when the six additional compounds that were also detected by the FID were included in the calculations, the average RSD value was lowered to $\pm$ 5.8 percent. Toluene exhibited the lowest RSD value ($\pm$ 1.8%) while tetrachloromethane produced the highest RSD value ($\pm$ 14.4%).

The background canister data, also shown in Table 6, follow the same trend as the spiked canister data. An average RSD value of $\pm$ 7.2 percent was found for the six compounds analyzed with the MSD, while an average RSD value of $\pm$ 3.6 percent was obtained with the ECD. With the FID detector system, the average RSD value was $\pm$ 8.5 percent. When the five additional FID detected compounds were included in the FID calculations, the average RSD value was lowered to $\pm$ 7.0 percent (chloroethene was not found in background air i.e. <0.1 ng/l).

TABLE 6. ANALYTICAL PRECISION DATA FROM REPLICATE ANALYSES OF SPIKED AND BACKGROUND CANISTERS

Compound	Spiked Canisters Detector Precision (± %)[a]			Background Canisters Detector Precision (± %)		
	MSD	ECD	FID	MSD	ECD	FID
Chloroethene	NM[b]	NM	7.4	NM	NM	NM
1,1,2-Trichloro-1,2,2-trifluoroethane	10.1	10.1	10.0	10.4	3.9	18.7
Trichloromethane	7.3	4.3	3.3	12.4	9.2	1.6
1,2-Dichloroethane	NM	NM	3.6	NM	NM	1.1
1,1,1-Trichloroethane	8.7	2.0	3.6	4.5	2.0	2.9
Benzene	NM	NM	1.6	NM	NM	3.6
Tetrachloromethane	6.4	1.3	14.4	4.9	1.7	15.1
Trichloroethene	7.3	2.8	11.9	8.6	2.7	7.2
Toluene	NM	NM	1.8	NM	NM	1.7
Tetrachloroethene	4.0	1.7	2.7	2.3	1.8	5.2
Chlorobenzene	NM	NM	2.9	NM	NM	15.2
1,2-Dimethylbenzene	NM	NM	6.7	NM	NM	4.9

(a) Detector precision is defined as the percent relative standard deviation.

(b) NM = not measured.

COMPARISON OF ECD AND MSD RESPONSES

The six compounds that were detected by both the electron capture and mass selective detectors were 1,1,2-trichloro-1,2,2-trifluoroethane, trichloromethane, 1,1,1-trichloroethane, tetrachloromethane, trichloroethene and tetrachloroethene. A comparison of concentrations obtained from replicate analyses of canisters and real time samples are shown in Tables 7-10. Tables 7 and 8 show the mean concentrations from the spiked and background canisters, while Tables 9 and 10 show the actual concentrations of the six compounds as determined during the real time sampling period. All four tables are organized by run number to reflect the fourteen sampling periods (run numbers 2 through 14). For each of the six compounds that were compared, the ECD concentration is given first followed by the MSD response. After each pair of concentrations, a percent relative difference is recorded. This value is defined as the difference between the ECD and MSD responses divided by the average response and then multiplied by 100. A negative percent relative difference value occurs whenever the MSD concentration is greater than the ECD value; a positive value indicates the opposite. A percent relative difference value with a "b" next to it indicates that either the ECD concentration has exceeded the linear range of the detector or that the data point is an outlier (greater than two standard deviations from the average relative difference value). For tetrachloromethane and tetrachloroethene non-linear behavior with the ECD occurred at concentrations above 20 ng/L. For trichloromethane, concentration values above 25 ng/L were non-linear. For the remaining three compounds, non-linear behavior resulted at ECD concentrations above 30 ng/L (for 1,1,2-trichloro-1,2,2-trifluoroethane and trichloroethene) and 35 ng/L (for 1,1,1-trichloroethane).

A summary of the average percent relative difference values from the three data sets is shown in Table 11. For 1,1,2-trichloro-1,2,2-trifluoroethane, negative average percent relative difference values were observed for all three data sets and indicated that the MSD recorded concentrations were in general higher than the corresponding ECD values. On the other hand, trichloromethane, tetrachloromethane and trichloroethene gave positive average percent relative difference values for all three

TABLE 7. ECD/MSD MEAN CONCENTRATIONS (ng/L) AND PERCENT RELATIVE DIFFERENCES OBTAINED FROM SPIKED CANISTERS(a)

RUN NUMBER	FREON 113 ECD.MEAN	FREON 113 MSD.MEAN	FREON 113 REL.DIFF	CHLORO-FORM ECD.MEAN	CHLORO-FORM MSD.MEAN	CHLORO-FORM REL.DIFF	1,1,1-TRI CHLOR. ECD.MEAN	1,1,1-TRI CHLOR. MSD.MEAN	1,1,1-TRI CHLOR. REL.DIFF
2	9.6	10.3	-7.0	4.7	2.8	50.7(b)	33.0	32.0	3.1
3	.	.	.	5.8	4.7	21.0	67.0	85.0	-23.7(b)
4	.	.	.	7.9	7.8	1.3	.	.	.
5	65.2	79.4	-19.6(b)	25.5	27.1	-6.1	30.2	34.8	-14.2
6	15.2	16.3	-7.0	12.1	9.0	29.4	70.7	64.0	9.9(b)
7	16.5	24.6	-39.4	4.6	3.6	24.4	5.2	4.5	14.4
8	7.1	8.5	-17.9	4.6	4.1	11.5	10.8	9.2	16.0
9	16.1	15.3	5.1	5.9	4.7	22.6	25.6	22.0	15.1
10	11.5	11.3	1.8	3.8	3.1	20.3	25.5	28.6	-11.5
11	.	.	.	6.6	7.0	-5.9	.	.	.
12	12.3	14.8	-17.1	4.3	4.7	-8.9	18.0	19.5	-8.0
13	10.5	11.8	-11.7	5.3	4.6	14.1	13.4	12.4	7.8
14	10.7	12.2	-13.1	4.2	4.8	-13.3	19.9	18.8	5.7
0			-12.6			12.4			1.3

RUN NUMBER	CARB. TETR CHLORIDE ECD.MEAN	CARB. TETR CHLORIDE MSD.MEAN	CARB. TETR CHLORIDE REL.DIFF	TRICHLORO ETHYLENE ECD.MEAN	TRICHLORO ETHYLENE MSD.MEAN	TRICHLORO ETHYLENE REL.DIFF	PERCHLORO ETHYLENE ECD.MEAN	PERCHLORO ETHYLENE MSD.MEAN	PERCHLORO ETHYLENE REL.DIFF	AVERAGE ABSOLUTE REL.DIFF
2	8.5	4.9	53.7	4.3	3.3	26.3	5.2	5.2	0.0	23.5
3	10.1	5.3	62.3	6.6	3.8	53.8	8.2	8.1	1.2	32.4
4	29.6	20.7	35.4(b)	.	.	.	8.5	8.0	6.1	14.2
5	34.4	37.2	-7.8(b)	28.4	23.7	18.0	33.5	40.0	-17.7(b)	13.9
6	8.9	4.4	67.7	5.2	3.6	36.4	5.8	5.5	5.3	25.9
7	4.6	4.0	14.0	3.9	4.6	-16.5	4.4	6.1	-32.4	23.5
8	4.3	3.6	17.7	4.1	3.7	10.3	4.8	4.8	0.0	12.2
9	4.4	4.0	9.5	3.9	2.7	36.4	4.1	3.7	10.3	16.5
10	4.3	3.7	15.0	3.9	4.2	-7.4	4.5	4.8	-6.5	10.4
11	16.6	14.9	10.8	.	.	.	5.6	5.6	0.0	5.6
12	5.1	4.9	4.0	14.5	14.3	1.4	6.9	9.3	-29.6	11.5
13	5.0	5.0	0.0	4.3	2.7	45.7	6.3	5.7	10.0	14.9
14	4.1	4.1	0.0	5.7	5.1	11.1	6.8	7.3	-7.1	8.4
0			21.7			19.6			-4.6	

(a) Percent relative difference = $\left(\frac{\text{ECD Response - MSD Response}}{\text{Average Response}}\right) \times 100.$

(b) These values are outliers or have exceeded the linear range of the ECD.

TABLE 8. ECD/MSD MEAN CONCENTRATIONS (ng/L) AND PERCENT RELATIVE DIFFERENCES OBTAINED FROM BACKGROUND CANISTERS(a)

RUN NUMBER	FREON 113 ECD.MEAN	FREON 113 MSD.MEAN	FREON 113 REL.DIFF	CHLORO-FORM ECD.MEAN	CHLORO-FORM MSD.MEAN	CHLORO-FORM REL.DIFF	1,1,1-TRI CHLOR. ECD.MEAN	1,1,1-TRI CHLOR. MSD.MEAN	1,1,1-TRI CHLOR. REL.DIFF
2	8.1	9.4	-14.9	0.8	0.9	-11.8	30.0	31.0	-3.3
3	37.4	42.0	-11.8(b)	2.5	1.5	50.0	67.0	81.0	-18.9
4	.	.	.	.	.	.	.	.	.
5	.	.	.	.	.	.	.	.	.
6	9.6	9.5	1.0	9.2	6.0	42.1	70.0	74.0	-5.6
7	1.4	1.5	-6.9	1.5	1.1	30.8	2.9	3.2	-9.8
8	1.8	.	.	2.9	.	.	9.3	.	.
9	11.4	11.6	-1.7	3.3	2.4	31.6	23.8	22.6	5.2
10	6.1	6.1	0.0	1.3	0.8	47.6	23.1	28.0	-19.2
11	.	.	.	.	.	.	.	.	.
12	6.3	6.7	-6.2	0.7	0.8	-13.3	16.2	17.8	-9.4
13	5.5	6.3	-13.6	2.5	4.5	-57.1	11.4	10.4	9.2
14	5.5	7.3	-28.1	1.1	5.4	-132.3(b)	18.9	19.4	-2.6
0			-9.1			-1.4			-8.0

RUN NUMBER	CARB. TETR CHLORIDE ECD.MEAN	CARB. TETR CHLORIDE MSD.MEAN	CARB. TETR CHLORIDE REL.DIFF	TRICHLORO ETHYLENE ECD.MEAN	TRICHLORO ETHYLENE MSD.MEAN	TRICHLORO ETHYLENE REL.DIFF	PERCHLORO ETHYLENE ECD.MEAN	PERCHLORO ETHYLENE MSD.MEAN	PERCHLORO ETHYLENE REL.DIFF	AVERAGE ABSOLUTE REL.DIFF
2	2.5	4.1	-48.5	1.4	0.7	66.7	1.1	1.1	0.0	24.2
3	2.3	1.2	62.9	3.4	1.7	66.7	3.4	3.1	9.2	36.5
4	.	.	.	.	.	.	.	.	.	.
5	.	.	.	.	.	.	.	.	.	33.4
6	2.0	0.9	75.9	2.0	1.3	42.4	1.4	.	.	15.1
7	1.0	0.9	10.5	1.0	0.8	22.2	0.9	1.0	-10.5	.
8	0.9	.	.	1.4	.	.	1.1	.	.	25.0
9	0.9	0.8	11.8	1.0	0.5	66.7	0.7	0.5	33.3	24.2
10	0.9	0.8	11.8	1.1	0.7	44.4	1.0	0.6	22.2	.
11	.	.	.	.	.	.	.	.	.	9.8
12	1.0	1.1	-9.5	12.7	12.5	1.6	1.9	2.3	-19.0	24.1
13	1.8	2.0	-10.5	1.5	1.1	30.8	2.4	1.9	23.3	47.6
14	1.0	3.0	-100.0	3.1	3.4	-9.2	3.5	4.0	-13.3	
0			0.5			36.9			5.6	

(a) Percent relative difference = $\left(\frac{\text{ECD Response - MSD Response}}{\text{Average Response}}\right) \times 100.$

(b) These values are outliers or have exceeded the linear range of the ECD.

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TABLE 9. ECD/MSD CONCENTRATIONS (ng/L) AND PERCENT RELATIVE DIFFERENCES OBTAINED DURING FIRST REAL TIME SAMPLING PERIOD WITH THE AUTOMATED GC SYSTEM(a)

RUN NUMBER	FREON 113 ECD	FREON 113 MSD	FREON 113 REL.DIFF	CHLORO-FORM ECD	CHLORO-FORM MSD	CHLORO-FORM REL.DIFF	1,1,1-TRI CHLOR. ECD	1,1,1-TRI CHLOR. MSD	1,1,1-TRI CHLOR. REL.DIFF
2	9.3	11.9	-24.5	4.5	3.4	27.8	34.0	35.0	-2.9
3	25.4	24.6	3.2	5.5	4.5	20.0	67.0	74.0	-9.9(b)
4	.	.	.	7.7	6.4	18.4	.	.	.
5	39.1	52.3	-28.9(b)	23.3	28.7	-20.8	26.0	29.6	-12.9
6	11.9	14.0	-16.2	8.2	7.9	3.7	55.0	63.0	-13.6(b)
7	3.1	4.1	-27.8	3.5	4.1	-15.8	4.3	4.0	7.2
8	3.7	4.7	-23.8	3.4	3.2	6.1	6.9	6.6	4.4
9	5.4	4.2	25.0	3.7	3.1	17.6	24.8	25.9	-4.3
10	8.3	9.6	-14.5	3.2	3.2	0.0	23.0	31.9	-32.4
11	.	.	.	5.9	6.8	-14.2	.	.	.
12	5.7	6.6	-14.6	3.0	4.0	-28.6	15.1	15.7	-3.9
13	10.4	11.6	-10.9	4.1	4.4	-7.1	13.3	10.4	24.5
14	8.0	10.2	-24.2	3.5	5.2	-30.1	12.4	12.2	1.6
0			-14.3			-2.4		28.0	-3.8

RUN NUMBER	CARB. TETR CHLORIDE ECD	CARB. TETR CHLORIDE MSD	CARB.TET CHLORIDE REL.DIFF	TRICHLORO ETHYLENE ECD	TRICHLORO ETHYLENE MSD	TRICHL ETHYL REL.DIFF	PERCHLORO ETHYLENE ECD	PERCHLORO ETHYLENE MSD	PERCHL ETHYL REL.DIFF	AVG.ABS REL.DIFF 1
2	9.2	3.9	80.8(b)	4.2	3.7	12.7	5.0	4.8	8.3	28.2
3	8.0	4.0	66.7	5.2	3.0	53.7	6.7	6.5	3.0	26.1
4	29.6	21.2	33.1(b)	.	.	.	9.5	8.5	11.1	20.9
5	32.8	28.6	13.7(b)	26.1	27.0	-3.4	33.5	44.7	-28.6(b)	18.1
6	8.3	4.2	65.6	4.4	2.9	41.1	5.4	.	.	28.0
7	4.2	3.6	15.4	3.4	2.9	15.9	4.1	5.7	-32.7	19.1
8	3.8	3.3	14.1	3.3	2.3	35.7	4.8	5.0	-8.3	15.4
9	3.6	4.0	-10.5	3.1	2.3	28.6	3.5	3.1	12.1	16.5
10	3.7	3.3	11.4	3.2	2.8	13.3	3.7	4.3	-15.0	14.5
11	12.2	.	.	.	.	.	5.9	4.7	22.6	16.4
12	4.0	3.7	7.8	23.0	19.8	15.0	5.5	7.5	-30.8	16.8
13	5.1	4.4	14.7	4.1	3.7	10.3	6.5	5.5	16.7	14.0
14	3.9	3.7	5.3	5.6	4.5	21.8	6.5	6.9	-6.0	16.3
0			26.5			22.3			-4.0	.

(a) Percent relative difference = $\left(\frac{\text{ECD Response - MSD Response}}{\text{Average Response}}\right) \times 100.$

(b) These values are outliers or have exceeded the linear range of the ECD.

TABLE 10. ECD/MSD CONCENTRATIONS (ng/L) AND PERCENT RELATIVE DIFFERENCES OBTAINED DURING SECOND REAL TIME SAMPLING PERIOD WITH THE AUTOMATED GC SYSTEM(a)

RUN NUMBER	FREON 113 ECD	FREON 113 MSD	FREON 113 REL.DIFF	CHLORO-FORM ECD	CHLORO-FORM MSD	CHLORO-FORM REL.DIFF	1,1,1-TRI CHLOR. ECD	1,1,1-TRI CHLOR. MSD	1,1,1-TRI CHLOR. REL.DIFF
2	5.2			5.4			30.0		
3	9.6	9.7	-1.0	3.8	2.9	26.9	56.0	50.0	11.3(b)
4				8.7					
5	40.8	82.8	-25.6(b)	24.2	27.2	-11.7	27.1	30.9	-13.1
6	9.7	10.0	-3.0	14.0	9.6	37.3	62.0	66.0	-6.3(b)
7	3.6	0.6	142.9(b)	4.6	3.1	38.0	5.6	3.4	48.9(b)
8	3.9	5.7	-37.5	4.9	4.6	6.3	13.6	12.6	9.1
9	24.9			6.6			22.8		
10	8.2	8.7	-5.9	3.4	2.6	26.7	22.9	27.3	-17.5
11				6.1	5.4	12.2			
12	10.9	12.3	-12.1	3.0	3.9	-26.1	17.3	15.9	8.4
13									4.6
14	7.4	8.2	-10.3	3.2	4.3	-29.3	24.4	23.3	5.7
0			5.9			9.0			

RUN NUMBER	CARB. TETR CHLORIDE ECD	CARB. TETR CHLORIDE MSD	CARB.TET CHLORIDE REL.DIFF	TRICHLORO ETHYLENE ECD	TRICHLORO ETHYLENE MSD	TRICHL ETHYL REL.DIFF	PERCHLORO ETHYLENE ECD	PERCHLORO ETHYLENE MSD	PERCHL ETHYL REL.DIFF	AVG. ABS REL. DIFF 2
2	7.7			3.9			4.8			
3	8.0	3.9	68.9	5.2	2.8	60.0	6.5	6.1	6.3	29.1
4	29.6						10.0			
5	33.4	30.0	10.7(b)	28.1	22.1	16.6	34.1	46.2	-30.1(b)	18.0
6	8.3	3.3	86.2	4.6	1.9	83.1(b)	5.3	5.4	-1.9	36.3
7	4.5	3.3	30.8	3.7	4.3	-15.0	4.1	5.4	-27.4	50.6
8	3.8	3.5	8.2	3.7	2.7	31.2	4.4	4.7	-6.6	16.5
9	3.8			3.2			3.4			
10	3.8	3.3	14.1	3.4	2.7	23.0	4.0	4.4	-9.5	16.1
11	12.3	14.2	-14.3				5.7			13.3
12	4.1	3.8	7.6	5.0	3.7	29.9	5.7	7.5	-27.3	16.6
13			5.3			42.4	8.0	6.4	-6.5	16.4
14	3.9	3.7	24.2	4.0	2.6	33.9			-12.9	
0										

(a) Percent relative difference = $\left(\frac{\text{ECD Response - MSD Response}}{\text{Average Response}}\right) \times 100$.

(b) These values are outliers or have exceeded the linear range of the ECD.

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TABLE 11. AVERAGE PERCENT RELATIVE DIFFERENCE VALUES OBTAINED BY COMPARING ELECTRON CAPTURE AND MASS SELECTIVE DETECTOR RESPONSES DURING THE FIELD STUDY[a]

Compound	Average Relative Difference Values (%)		
	Spiked Canisters	Background Canisters	Real Time Samples
1,1,2-Trichloro-1,2,2-trifluoroethane	-11.8	-8.8	-12.4
Trichloromethane	9.2	15.0	2.2
1,1,1-Trichloroethane	3.2	-6.0	-1.9
Tetrachloromethane	23.2	0.5	23.4
Trichloroethene	19.6	36.9	24.1
Tetrachloroethene	-3.6	5.7	-5.1

(a) Percent relative difference values = $\left(\frac{\text{ECD Response - MSD Response}}{\text{Average Response}}\right) \times 100.$

data sets. The positive values denoted higher relative ECD responses for these three compounds. Tetrachloroethene and 1,1,1-trichloroethane showed no consistent bias. The spiked canister and real time sampling data showed very similar percent relative difference values as one would expect since both types of sampling were carried out downstream of the sample spiking port. Although the same general trend is also observed with the background canister data, the somewhat larger variation resulted because these samples were collected upstream of the spiking port and therefore generally contained much lower concentrations of the six target compounds.

TENAX GC ADSORBENT VERSUS WHOLE AIR COLLECTION/CRYOGENIC PRECONCENTRATION COMPARISON STUDY FOR AMBIENT AIR

In order to compare the performance of the two methods for sampling the fifteen "spiked" compounds in ambient air, a series of parallel sampling experiments was conducted as described in the experimental section as well as in a companion report (3). For comparison purposes, thirteen sampling runs were completed (see Table 3). Run numbers 4 and 11 were clean air experiments using a diluted mixture from an audit cylinder supplied by EPA, and run number 5 was a similar run using a diluted mixture from the calibration cylinder described in the experimental section. Results using the dilute audit and calibration mixtures are discussed in later portions of the report; the following discussion will focus on the data from the ten "spiked" ambient air sampling runs.

For each sampling run a series of four Tenax GC adsorbent samples (nominally 5, 10, 10 and 20 liters) were collected over a two-hour period from the spiked portion of the sampling manifold. Simultaneously, integrated canister samples were also collected for later analysis by the cryogenic trapping/GC system. In order to compare the data from the two collection methods, the appropriate Tenax GC concentration values were ratioed to the corresponding concentrations found by cryogenic trapping/GC analysis of canister samples. The ratios provided a direct measure of the relative recovery of the Tenax GC adsorbent for each compound. The comparison was done on this basis because the canister/cryogenic trapping

concentrations generally agreed better with the diluted concentration generated in the manifold (next section). Likewise literature data has shown that several of the fifteen target compounds have low breakthrough volumes on Tenax GC and are therefore not efficiently collected (5).

In Figure 6 a typical scatterplot is shown depicting concentration ratios for benzene from spiked ambient air runs (ratio is concentration value from Tenax divided by the value obtained using canister sampling technique). In Table 12 a summary of the performance data for Tenax GC relative to canister/cryogenic trapping is given. Each compound is listed along with its breakthrough volume and the average Tenax GC recovery relative to canister/cryogenic trapping obtained over the ten sampling runs. As indicated in the table for those compounds in which breakthrough volumes were very low, the nominally 5 liter Tenax GC adsorbent sample was used in the comparisons; the remaining concentration values were taken from the 10 liter samples. The values used for the canister samples were obtained using the mass selective detector, because this detection system was less subject to potential interferences (concentration data is tabulated in Appendix A). However, the toluene and 1,2-dimethylbenzene values were obtained using FID due to limitations on the number of ions which could be monitored using the mass selective detector.

For the compounds, chloroethene and 1,1-dichloroethene, no meaningful data was obtained with the Tenax GC adsorbent. With the exception of the anomalous behavior of 1,1,2-trichloro-1,2,2-trifluoroethane, the compounds dichloromethane through trichloroethene gave very reasonable relative recoveries ranging from 83 to 130 percent. However a dramatic fall off in recovery is observed for the less volatile compounds, toluene, tetrachloroethene, chlorobenzene and 1,2-dimethylbenzene. The reason for the relatively low recoveries for these higher boiling compounds is unclear. Re-examination of the system apparatus indicated that adequate desorption temperatures (~250^{o}C) were always maintained. The possibility of compound adsorption onto the walls of the manifold/tubing prior to the adsorbent tube was also ruled out by interchanging sampling lines to the two collection methods.

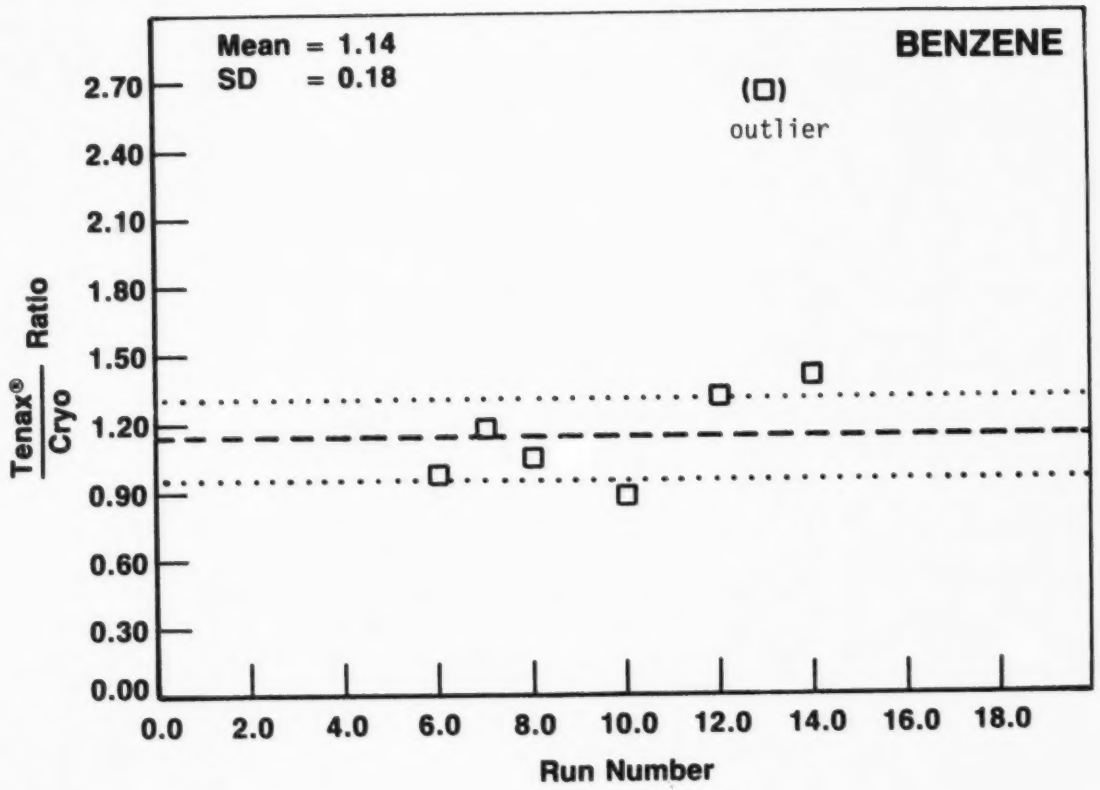

Figure 6. Scatterplot of concentration ratios for benzene from spiked ambient air runs (ratio is concentration value from Tenax divided by the value obtained using canister sampling technique).

TABLE 12. PERFORMANCE DATA FOR TENAX RELATIVE TO CRYOGENIC TRAPPING/GC ANALYSIS OF CANISTER SAMPLES

Compound	Tenax GC Breakthrough Volume[a], Liters/Cartridge	Average Tenax GC Recovery Relative To Cryogenic Trapping, %
Chloroethene	0.8	(b)
1,1-Dichloroethene	Not Given	(b)
Dichloromethane	4	83(21)[d]
3-Chloropropene[c]	6	87(35)
1,1,2-Trichloro-1,2,2-trifluoroethane	Not Given	39(25)
Trichloromethane[c]	13	100(36)
1,2-Dichloroethane[c]	18	100(15)
1,1,1-Trichloroethane[c]	9	130(42)
Benzene	27	110(18)
Tetrachloromethane[c]	13	110(37)
Trichloroethene	28	112(26)
Toluene	122	70(19)
Tetrachloroethene	106	88(27)
Chlorobenzene	249	78(35)
1,2-Dimethylbenzene	334	55(21)

(a) Data from Reference 5 at 90°F.

(b) No meaningful data obtained.

(c) Low volume (nominally 5 liters) Tenax GC value used for these compounds. Medium volume (nominally 10 liters) Tenax GC value used for all other compounds.

(d) Value in parentheses is standard deviation for all sampling runs (excluding audit and calibration cylinder sampling runs).

(e) Value for ethylbenzene.

TENAX GC ADSORBENT VERSUS WHOLE COLLECTION/ CRYOGENIC PRECONCENTRATION COMPARISON STUDY FOR SPIKED HIGH PURITY AIR

As mentioned previously, sampling runs 4 and 11 utilized an audit cylinder containing several of the target compounds spiked into a high purity air stream flowing through the same manifold as was employed for the ambient air experiments. Data from the analysis of a dilution mixture of the audit cylinder are provided in Table 13. The expected concentration values shown in the table result from a 0.0099 dilution of the audit cylinder. The undiluted concentration values in the audit cylinder were determined by EPA. As expected, Tenax adsorbent showed low recovery for chloroethene, where as chloroethene data from the canister sampling compared very well with concentrations measured by EPA. For the remaining compounds a good deal of variation in compound concentrations occurs for both sampling runs. However in comparing the average concentration values from both runs with values supplied by EPA, agreement within $\pm$ 20 percent is generally obtained. Much better agreement is observed when comparing the analyses of the undiluted audit cylinder. These results are shown in Table 14. For the direct analysis of the audit cylinder agreement between laboratories is within $\pm$ 5 percent.

Data for the calibration cylinder are presented in Table 15. These data clearly indicate that cryogenic trapping provides the best recovery for each of the target compounds, except for the high (230%) recovery observed for 1,1,2-trichloro-1,2,2-trifluoroethane. The reason for the much lower recoveries for the higher boiling compounds (e.g., toluene, chlorobenzene, and 1,2-dimethylbenzene) for Tenax GC is not clear; because somewhat better recoveries were observed in the ambient air studies.

TABLE 13. RESULTS OF ANALYSIS OF A DILUTION MIXTURE FROM RTI AUDIT CYLINDER NO. ALL 11933 (ng/L at 25°C, 1 atm)

Compound	Expected(a) Concentration	Run No. 4 (07/20/84)		Run No. 11 (08/03/84)		Average	
		Canister	Tenax	Canister	Tenax	Canister	Tenax
Chloroethene	10.2	9.9	0.7	9.4	--	9.7	--
Trichloromethane	6.1	7.8	8.1	7.0	7.5	7.4	7.8
Benzene	11.8	16.0	9.4	9.4	12.0	12.7	10.7
Tetrachloromethane	22.3	21.0	17.0	15.0	19.0	18.0	18.0
Tetrachloroethene	7.5	8.0	8.5	5.6	8.0	6.8	8.3

(a) Expected concentration is based upon a 0.0099 dilution of an audit cylinder. Original concentrations were provided by EPA.

TABLE 14. RESULTS OF ANALYSIS OF RTI AUDIT CYLINDER NO. AAL 11933 (ng/mL at 25°C, 1 atm)

Compound	EPA Analysis	Battelle Analysis		
	GC/FID	GC/FID	GC/MS	Average
Chloroethene	1.03	1.00	1.00	1.00
Trichloromethane	0.62	0.69	0.61	0.65
Benzene	1.19	1.16	1.22	1.19
Tetrachloromethane	2.25	2.30	2.00	2.15
Tetrachloroethene	0.76	0.80	0.76	0.78

TABLE 15. RESULTS OF ANALYSIS OF A DILUTION MIXTURE FROM BATTELLE'S CALIBRATION CYLINDER (Run 5, 07/20/84)

Compound	Expected Concentration, ng/L	Percent Recovery[a]	
		Cryogenic Trapping	Tenax GC
Chloroethene[b]	26	103	8.3
1,1-Dichloroethene[b]	17	112	55
Dichloromethane[b]	13	107	360
3-Chloropropene[b]	19	95	79
1,1,2-Trichloro-1,2,2,-trifluoroethane[b]	34	230	47
Trichloromethane[b]	27	100	104
1,2-Dichloroethane[b]	24	120	96
1,1,1-Trichloroethane[b]	30	117	89
Benzene	15	93	73
Tetrachloromethane[b]	36	103	89
Trichloroethene	27	89	76
Toluene	18	90	50
Tetrachloroethene	34	118	65
Chlorobenzene	22	118	43
1,2-Dimethylbenzene	20	120	23

(a) Average for duplicate samples.

(b) Low volume (nominally 5 liters) Tenax GC value used for these compounds. Medium volume (nominally 10 liters) Tenax GC value used for all other compounds.

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APPENDIX A

CONCENTRATION DATA FOR TENAX AND CANISTER/CRYOGENIC TRAPPING COMPARISON

TABLE A-1. CONCENTRATION DATA FOR RUN NUMBER 2, AMBIENT AIR 07/17/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.5	8.5	18.5	
Compound				
Chloroethene	ND[a]	ND	ND	NM[c]
Acrylonitrile	1.5	0.3	0.4	NM
1,1-Dichloroethene	1.2	0.4	0.5	NM
Dichloromethane	24.0	11.5(2.12)	9.9	NM
3-Chloropropene	2.2	0.9(0.21)	1.1	NM
Trichlorotrifluoroethane	3.0	1.4(0.21)	1.0	10.3(1.41)
Trichloromethane	2.7	2.0(0.35)	2.4	2.8(0.00)
1,2-Dichloroethane	2.2	1.4(0.49)	2.0	NM
1,1,1-Trichloroethane	28.5	18.5(1.41)	22.5	32.0(1.41)
Benzene	4.8	3.9(0.49)	4.5	NM
Tetrachloromethane	2.6	2.0(0.14)	2.7	4.9(0.14)
Trichloroethylene	3.2	2.6(0.57)	3.1	3.3(0.14)
Toluene	6.9	5.9(1.41)	7.6	15.8(0.00)
Tetrachloroethene	3.0	2.5(0.64)	1.2	5.2(0.14)
Chlorobenzene	1.5	1.0(0.33)	1.4	NM
1,2-Dimethylbenzene	2.8	1.6(0.28)	1.3	6.9(0.71)

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-2. CONCENTRATION DATA FOR RUN NUMBER 3, AMBIENT AIR 07/19/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.6	9.4	18.2	
Compound				
Chloroethene	ND[a]	ND	ND	NM[c]
Acrylonitrile	1.1	0.8(0.25)	0.5	NM
1,1-Dichloroethene	1.8	1.4(0.14)	0.8	NM
Dichloromethane	28.0	13.5(0.71)	5.9	NM
3-Chloropropene	ND	2.3	1.1	NM
Trichlorotrifluoroethane	8.6	4.8(0.07)	1.9	NM
Trichloromethane	4.0	3.4(0.21)	2.9	4.7(0.14)
1,2-Dichloroethane	3.0	2.6(0.42)	1.9	NM
1,1,1-Trichloroethane	78.0	57.5(10.6)	35.0	85.0(1.41)
Benzene	Saturated	Saturated	Saturated	Saturated
Tetrachloromethane	6.0	5.2(0.92)	4.6	5.3(0.14)
Trichloroethylene	2.7	3.8(1.20)	4.3	3.8(0.14)
Toluene	12.0	10.4(2.33	13.0	22.5(0.42)
Tetrachloroethene	6.1	5.1(0.85)	3.2	8.1(0.14)
Chlorobenzene	2.3	2.0(0.49)	1.8	NM
1,2-Dimethylbenzene	4.2	3.4(0.49)	2.4	7.7(0.14)

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-3. CONCENTRATION DATA FOR RUN NUMBER 4, AUDIT CYLINDER 07/20/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.5	9.1	18.2	
Compound				
Chloroethene	Sample Lost	0.7(0.28)	0.3	9.4(1.27)
Acrylonitrile	"	ND[a]	ND	NM
1,1-Dichloroethene	"	ND	ND	NM
Dichloromethane	"	ND	ND	NM
3-Chloropropene	"	ND	ND	NM
Trichlorotrifluoroethane	"	3.4(1.20)	1.8	NM
Trichloromethane	"	8.1(0.28)	5.9	7.8(0.71)
1,2-Dichloroethane	"	ND	ND	NM
1,1,1-Trichloroethane	"	ND	ND	NM
Benzene	"	9.4(0.35)	7.9	17.5(1.41)
Tetrachloromethane	"	17.0	15.0	20.7(1.98)
Trichloroethylene	"	ND	ND	NM
Toluene	"	ND	ND	NM
Tetrachloroethene	"	8.5(0.28)	6.4	8.0(0.71)
Chlorobenzene	"	ND	ND	NM
1,2-Dimethylbenzene	"	ND	ND	NM

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-4. CONCENTRATION DATA FOR RUN NUMBER 5, CALIBRATION CYLINDER 07/24/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.5	9.4	18.1	
Compound				
Chloroethene	2.1	1.0(1.15)[a]	0.8	26.7
Acrylonitrile	1.0	1.9(0.78)	2.7	NM[b]
1,1-Dichloroethene	9.3	7.0(0 64)	5.5	18.9
Dichloromethane	46.7	10.0(4.31)	5.8	14.3
3-Chloropropene	15.0	12.2(4.03)	11.0	18.2
Trichlorotrifluoroethane	16.0	9.4(3.75)	7.0	79.4
Trichloromethane	28.0	23.5(4.95)	23.0	27.1
1,2-Dichloroethane	23.0	18.5(2.12)	18.0	28.9
1,1,1-Trichloroethane	33.6	25.8(5.66)	24.9	34.8
Benzene	12.7	10.9(1.41)	10.9	14.0
Tetrachloromethane	32.0	26.0(5.66)	28.0	37.2
Trichloroethylene	26.0	20.5(2.12)	13.0	23.7
Toluene	10.9	9.0(0.35)	9.0	20.1(0.30)
Tetrachloroethene	25.0	22.0(1.41)	15.0	40.0
Chlorobenzene	11.8	9.4(0.35)	7.5	26.4
1,2-Dimethylbenzene	5.1	4.6(0.28)	3.6	23.8(0.30)

a. Value in parentheses is standard deviation for duplicate samples.
b. NM = Not Measured.

TABLE A-5. CONCENTRATION DATA FOR RUN NUMBER 6, AMBIENT AIR 07/26/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.6	8.7	18.3	
Compound				
Chloroethene	ND[a]	ND	ND	2.5
Acrylonitrile	0.3	0.4(0.16)	0.2	NM[c]
1,1-Dichloroethene	2.4	1.2(0.14)	0.4	1.8
Dichloromethane	22.7	18.8(2.83)	12.4	32.0
3-Chloropropene	2.4	1.5(0.00)	0.6	2.5
Trichlorotrifluoroethane	7.9	3.6(0.28)	1.8	16.3
Trichloromethane	11.0	8.9(0.92)	7.3	9.0
1,2-Dichloroethane	2.2	2.5(0.35)	1.8	2.4
1,1,1-Trichloroethane	60.6	57.8(2.83)	46.9	64.0
Benzene	41.7	47.8(5.66)	36.9	49.0
Tetrachloromethane	3.4	4.0(0.57)	2.9	4.4
Trichloroethylene	3.3	2.9(1.48)	1.5	3.6
Toluene	9.9	10.2(1.06)	10.0	20.3(0.60)
Tetrachloroethene	3.6	3.5(0.14)	3.2	5.5
Chlorobenzene	0.9	1.1(0.00)	1.3	3.3
1,2-Dimethylbenzene	1.2	1.7(0.14)	1.1	6.0(0.40)

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-6. CONCENTRATION DATA FOR RUN NUMBER 7, AMBIENT AIR 07/26/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.6	8.7	18.4	
Compound				
Chloroethene	ND[a]	ND	ND	2.4
Acrylonitrile	0.9	0.8(0.49)	0.1	NM[c]
1,1-Dichloroethene	2.1	1.2(0.28)	0.3	1.9
Dichloromethane	0.3	1.1(1.34)	0.1	3.1
3-Chloropropene	2.0	2.3(1.34)	0.7	1.9
Trichlorotrifluoroethane	1.6	1.9(0,49)	0.4	24.6
Trichloromethane	1.3	1.0(0.03)	0.4	3.6
1,2-Dichloroethane	5.7	3.7(4.24)	1.0	2.6
1,1,1-Trichloroethane	8.9	5.6(0.00)	1.3	4.5
Benzene	8.9	5.7(0.99)	1.1	4.8
Tetrachloromethane	5.2	3.6(0.7)	1.1	4.0
Trichloroethylene	6.8	4.7(0.21)	2.0	4.6
Toluene	10.9	10.6(3.39)	2.8	12.0(0.71)
Tetrachloroethene	5.3	4.7(1.56)	0.8	6.1
Chlorobenzene	2.5	2.2(0.78)	0.3	2.5
1,2-Dimethylbenzene	2.9	2.0(0.28)	0.4	4.5(0.07)

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-7. CONCENTRATION DATA FOR RUN NUMBER 8, AMBIENT AIR 07/30/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.4	9.2	18.4	
Compound				
Chloroethene	0.3	ND[a]	ND	2.3
Acrylonitrile	0.6	0.3(0.20)	0.3	NM[c]
1,1-Dichloroethene	0.8	0.5(0.24)	0.4	1.7
Dichloromethane	11.7	10.9(0.74)	9.0	12.5
3-Chloropropene	1.5	1.1(0.40)	0.8	2.3
Trichlorotrifluoroethane	1.5	0.7(0.16)	0.6	8.5(0.07)
Trichloromethane	4.3	3.3(0.35)	3.6	4.1(0.07)
1,2-Dichloroethane	2.8	2.5(0.25)	2.7	2.5
1,1,1-Trichloroethane	11.4	9.5(1.70)	11.2	9.2(0.07)
Benzene	4.7	4.2(0.23)	4.6	4.0
Tetrachloromethane	4.0	2.5(0.24)	2.7	3.6(0.06)
Trichloroethylene	4.7	4.1(0.03)	4.3	3.7(0.21)
Toluene	10.2	8.2(0.74)	7.9	12.1(0.03)
Tetrachloroethene	5.6	5.0(0.47)	5.3	4.8(0.04)
Chlorobenzene	3.8	3.0(0.14)	2.7	2.6
1,2-Dimethylbenzene	5.5	4.2(0.17)	3.4	5.3(0.18)

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-8. CONCENTRATION DATA FOR RUN NUMBER 9, AMBIENT AIR 07/31/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.6	8.6	19.0	
Compound				
Chloroethene	ND[a]	ND	ND	2.7
Acrylonitrile	1.1	0.3(0.59)	0.3	NM[c]
1,1-Dichloroethene	3.1	1.0(0.20)	0.4	2.0
Dichloromethane	49.8	23.6(0.79)	11.3	59.2
3-Chloropropene	3.6	1.6(0.23)	1.0	2.3
Trichlorotrifluoroethane	15.0	6.8(1.53)	3.0	15.3(2.26)
Trichloromethane	7.0	5.3(0.34)	4.0	4.7(0.06)
1,2-Dichloroethane	4.3	3.3(0.24)	3.0	4.0
1,1,1-Trichloroethane	38.6	26.4(1.29)	23.6	22.0(2.26)
Benzene	No Data	No Data	No Data	4.4
Tetrachloromethane	4.1	3.6(0.01)	2.5	4.0(0.00)
Trichloroethylene	5.4	3.7(0.13)	3.6	2.7(0.21)
Toluene	15.3	14.5(0.79)	14.7	14.6(0.14)
Tetrachloroethene	4.3	3.7(0.44)	1.6	3.7(0.00)
Chlorobenzene	3.3	2.2(0.11)	2.2	3.3
1,2-Dimethylbenzene	4.1	3.3(0.06)	2.6	4.8(0.20)

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-9. CONCENTRATION DATA FOR RUN NUMBER 10, AMBIENT AIR 08/02/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.8	9.3	18.7	
Compound				
Chloroethene	0.8	ND[a]	ND	2.7
Acrylonitrile	1.0	0.7(0.03)	0.4	NM
1,1-Dichloroethene	7.5	0.9(0.00)	0.4	1.8
Dichloromethane	26.4	17.5(1.50)	10.3	33.0
3-Chloropropene	2.5	2.0(0.27)	0.9	NM
Trichlorotrifluoroethane	4.3	2.3(0.37)	1.2	11.3(0.10)
Trichloromethane	1.7	3.9(0.20)	3.1	3.1(0.03)
1,2-Dichloroethane	2.9	2.8(0.06)	2.2	2.9
1,1,1-Trichloroethane	22.2	33.0(0.34)	23.3	28.6(4.24)
Benzene	15.4	10.9(0.06)	11.0	12.2
Tetrachloromethane	3.1	3.7(0.28)	3.2	3.7(0.03)
Trichloroethylene	3.8	3.5(0.11)	3.5	4.2(0.03)
Toluene	13.7	12.3(0.31)	14.1	16.6(0.05)
Tetrachloroethene	5.3	4.8(0.14)	3.0	4.8(0.03)
Chlorobenzene	2.0	1.9(0.11)	2.2	4.3
1,2-Dimethylbenzene	3.6	2.8(0.23)	3.0	6.7(0.07)

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-10. CONCENTRATION DATA FOR RUN NUMBER 11, AUDIT CYLINDER 08/03/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	5.1	9.4	18.4	
Compound				
Chloroethene	ND[a]	0.1(0.14)[b]	0.1	9.4
Acrylonitrile	ND	0.0(0.01)	ND	NM
1,1-Dichloroethene	ND	0.0	ND	NM
Dichloromethane	ND	ND	ND	NM
3-Chloropropene	ND	0.0	ND	NM
Trichlorotrifluoroethane	0.2	0.0	ND	NM
Trichloromethane	7.0	7.5(1.10)	7.1	7.0(0.07)
1,2-Dichloroethane	ND	0.0(0.06)	0.1	NM
1,1,1-Trichloroethane	0.8	0.3(0.06)	0.3	0.5(0.07)
Benzene	11.2	11.5(1.02)	11.6	9.4
Tetrachloromethane	17.4	18.6(0.65)	18.5	14.9(0.06)
Trichloroethylene	0.9	0.5(0.11)	0.5	NM
Toluene	3.4	3.6(0.04)	3.1	2.7(0.06)
Tetrachloroethene	6.6	8.0(1.00)	8.1	5.6(0.07)
Chlorobenzene	0.3	0.3(0.08)	0.3	NM
1,2-Dimethylbenzene	1.1	1.0(0.01)	1.0	NM

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-11. CONCENTRATION DATA FOR RUN NUMBER 12, AMBIENT AIR 07/06/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.6	9.4	18.4	
Compound				
Chloroethene	ND[a]	ND	ND	3.1
Acrylonitrile	1.6	1.2(0.03)	0.7	NM
1,1-Dichloroethene	1.7	1.2(0.23)	0.6	2.2
Dichloromethane	9.9	11.5(7.67)	4.2	22.6
3-Chloropropene	1.8	1.7(0.40)	1.1	2.1
Trichlorotrifluoroethane	5.6	3.0(0.06)	1.6	14.6(0.10)
Trichloromethane	4.6	3.7(0.41)	3.3	4.7(0.04)
1,2-Dichloroethane	3.4	3.3(0.57)	3.3	4.4
1,1,1-Trichloroethane	25.1	22.2(2.25)	19.5	19.5(0.10)
Benzene	9.1	7.2(0.85)	9.7	5.5
Tetrachloromethane	4.7	3.8(0.28)	4.7	4.9(0.04)
Trichloroethylene	19.3	15.9(1.80)	15.1	14.3(1.70)
Toluene	16.5	15.8(2.15)	16.6	21.1(0.15)
Tetrachloroethene	7.7	6.1(0.57)	3.8	9.3
Chlorobenzene	4.3	3.4(0.42)	3.3	3.6
1,2-Dimethylbenzene	6.9	5.0(0.44)	3.7	7.9(0.07)

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.

TABLE A-12. CONCENTRATION DATA FOR RUN NUMBER 13, AMBIENT AIR 08/07/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.5	8.5	18.1	
Compound				
Chloroethene	0.1	0.1(0.04)[a]	0.1	2.5
Acrylonitrile	2.3	1.3(0.11)	0.8	NM
1,1-Dichloroethene	2.0	1.3(0.03)	0.7	5.1
Dichloromethane	22.6	12.7(3.76)	5.8	17.5
3-Chloropropene	3.4	2.1(0.38)	1.3	7.3
Trichlorotrifluoroethane	3.7	2.7(0.11)	1.4	11.8(0.04)
Trichloromethane	7.2	5.7(0.14)	4.2	4.6(0.06)
1,2-Dichloroethane	4.5	3.7(0.01)	3.0	3.8
1,1,1-Trichloroethane	20.2	15.6(0.57)	12.3	12.4(2.12)
Benzene	10.6	8.5(1.98)	5.9	3.2
Tetrachloromethane	8.6	6.0(14.0)	3.9	5.0(0.06)
Trichloroethylene	6.5	6.0(0.54)	4.7	2.7(0.04)
Toluene	20.0	18.2(1.81)	17.2	21.8(0.03)
Tetrachloroethene	10.6	8.1(0.23)	4.7	5.7(0.01)
Chlorobenzene	5.8	4.6(0.03)	3.7	3.2
1,2-Dimethylbenzene	9.2	6.8(0.18)	5.1	8.9(1.00)

a. Value in parentheses is standard deviation for duplicate samples.
b. ND = Not Detected.
c. NM = Not Measured.

TABLE A-13. CONCENTRATION DATA FOR RUN NUMBER 14, AMBIENT AIR 08/09/84

	Low Tenax®	Medium Tenax®	High Tenax®	Cryogenic Spiked
Average Sampling Volume, Liters	4.6	8.6	19.8	
Compound				
Chloroethene	0.2	ND[a]	Sample Lost	2.5
Acrylonitrile	1.9	1.2(0.01)[b]	"	NM[c]
1,1-Dichloroethene	2.6	1.4(0.20)	"	6.1
Dichloromethane	24.3	16.7(1.33)	"	31.9
3-Chloropropene	4.4	2.6(0.03)	"	8.5
Trichlorotrifluoroethane	5.0	2.6(0.01)	"	12.2(2.69)
Trichloromethane	5.9	5.1(0.28)	"	4.8(0.31)
1,2-Dichloroethane	4.3	3.8(0.01)	"	3.4
1,1,1-Trichloroethane	34.0	30.4(1.80)	"	18.8(2.97)
Benzene	16.0	11.4(2.55)	"	8.1
Tetrachloromethane	7.1	5.0(2.90)	"	4.1(0.08)
Trichloroethylene	10.1	8.2(0.54)	"	5.1(0.01)
Toluene	19.8	17.2(1.13)	"	20.1(0.90)
Tetrachloroethene	9.2	8.3(0.14)	"	7.3
Chlorobenzene	5.6	4.3(0.06)	"	2.8
1,2-Dimethylbenzene	9.6	6.9(0.72)	"	8.0(1.40)

a. ND = Not Detected.
b. Value in parentheses is standard deviation for duplicate samples.
c. NM = Not Measured.